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A HANDBOOK

OF

VOLUMETRIC ANALYSIS.

DESIGNED FOR

THE USE OF CLASSES IN COLLEGES AND
TECHNICAL SCHOOLS.

BY

EDWARD HART, S.B.,

FELLOW OF CHEMISTRY IN THE JOHNS HOPKINS UNIVERSITY.

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PREFACE.

THIS volume is intended for a handbook for the use of those who are much occupied with volumetric work. The methods described are most of them general, and have been carefully selected and brought up to date. It is believed that few valuable processes have been omitted. In most cases where from the scope of the book brevity is necessary, references to further and more extended sources of information are appended.

Part I. contains directions for the selection of apparatus, correction of errors, preparation of solutions, etc.

Part II. is devoted to the methods of estimating the elements and their more important compounds.

Part III. contains a few cases of the application of methods described in Part II.

Thanks are due Mr. W. E. Du Bois, Assayer of the Mint at Philadelphia, and Prof. Koenig, of the University of Pennsylvania, for information received. Much valuable work has been done in the past few years in the application of the spectroscope to volumetric work. For an account of the progress made in this direction, the following works may be consulted: Vogel's "Practische Spectralanalyse Irdischer Stoffe, Nördlingen, 1877," Vierordt's "Die Quantitative Spectralanalyse in ihrer Anwendung auf Physiologie, Physik, Chemie und Technologie, Tübingen, 1876."

EDWARD HART.

BALTIMORE, January, 1878.

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TABLE OF ATOMIC WEIGHTS.

Aluminum	Al	27·4	Manganese	Mn	55·
Antimony	Sb	122·	Mercury	Hg	200·
Arsenic	As	75·	Molybdenum	Mo	95·8
Barium	Ba	137·	Nickel	Ni	58·8
Bismuth	Bi	210·	Nitrogen	N	14·044
Boron	B	11·	Oxygen	O	16·
Bromine	Br	79·952	Palladium	Pd	106·48
Cadmium	Cd	112·	Phosphorus	P	31·
Calcium	Ca	40·	Platinum	Pt	197·4
Carbon	C	12·	Potassium	K	39·137
Chlorine	Cl	35·457	Silicon	Si	28·
Chromium	Cr	52·48	Silver	Ag	107·93
Cobalt	Co	58·8	Sodium	Na	23·043
Copper	Cu	63·17	Strontium	Sr	87·5
Gold	Au	196·67	Sulphur	S	32·
Hydrogen	H	1·	Tin	Sn	118·
Iodine	I	126·85	Titanium	Ti	50·
Iron	Fe	56.	Tungsten	W	184·
Lead	Pb	206·92	Uranium	U	118·8
Magnesium	Mg	24·	Zinc	Zn	65·13

PART I.

INTRODUCTORY.

When we analyze a substance volumetrically, we pay attention to the volume of a solution of known strength which must be added to it to perform a certain reaction. The exact moment when a sufficient quantity of the solution has been added is known by changes which are visible to the eye, but are different in different cases, and depend upon the nature of the substance to be estimated and the solution used. Sometimes a third substance must be added to show an excess of the reagent, and in this case the appearance which marks the completion of the analysis is called the end reaction. The indications by which we know analyses to be finished may be classed as follows:

1. A change in color of the titrated solution.
2. The point when a precipitate ceases to form.
3. The formation of a precipitate in the whole solution, or the formation of a precipitate or color in a portion which is dipped out and tested with an appropriate reagent.
4. The re-solution of a precipitate.

To the first class belong all acidimetric and alka-

3. *Precipitation.*—Under this head are classed those reactions in which the substance is, 1st, thrown down completely by an appropriate reagent; 2d, the reagent is added until a precipitate makes its appearance; or, 3d, the reagent added to a solution containing a suspended precipitate until this redissolves. Whatever the change brought about, it must be a chemical one and of a definite character, and must take place rapidly. If the reaction produced is influenced greatly by the strength of the solution or the temperature, it is of doubtful value, and only to be used when these conditions can be made the same in all instances.

Beside the apparatus used for gravimetric analysis, we need for volumetric work, apparatus for measuring the exact volume of solutions used, for preparing and keeping solutions, and for some other special purposes.

THE INSTRUMENTS.

THE BALANCES.

As the balance is the final resort in all analysis, volumetric as well as gravimetric, it is important that its accuracy and sensibility be ascertained before it is used. Two balances are needed—an analytical balance capable of carrying 100 gms. in each pan and turning with $\frac{1}{10}$ mgr. with this load, and a larger one carrying 2 to 5 kilogrammes and turning with 5 mgr. with its full charge. The smaller balance is used for weighing out accurately small quantities of substance for analysis, etc.; the larger one for graduating litre flasks and for weighing roughly large quantities of chemicals.

THE BURETTE.

Many different forms of burette have been proposed, adapted for special purposes, or for which the inventors claim especial excellence. They are all constructed on the same general principle, however, and consist essentially of a perfectly cylindrical glass tube, of equal diameter throughout, divided into cubic centimetres and fractions thereof. The scale is usually etched or ground upon the outer surface of the glass. The modifications in the form of the burette spoken of above have reference to the mode of securing the best delivery of the fluid. It is necessary that the apparatus for this purpose shall allow the liquid to flow either in a continuous stream or in small drops, at the pleasure of the analyst, and that the flow may be easily and quickly adjusted. The burette most generally used is that of Mohr, which is simple, convenient, and cheap. It consists of a straight tube drawn out at the lower end, the drawn-out portion having such a shape that a piece of rubber tubing slipped over it will adhere firmly without any other fastening.

This drawn-out portion is shown in the accompanying figure. A short piece of rubber tubing is slipped over this, and into its lower end a drawn-out glass tube with a fine aperture inserted. In this condition the liquid in the burette would flow from the point in a fine stream. For regulating this flow, a pinch-cock, shown in Fig. 3, is slipped over the rubber tube. When the pressure is entirely removed, the pinch-cock presses the walls of the tube together, making a perfectly tight joint, Fig. 2. Another method of regulating the flow is by slipping a piece of glass rod about 1 centimetre long inside the rubber tube between the burette point and the delivery tube, as in Fig. 4.

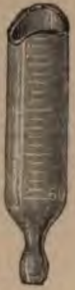

FIG. 1.

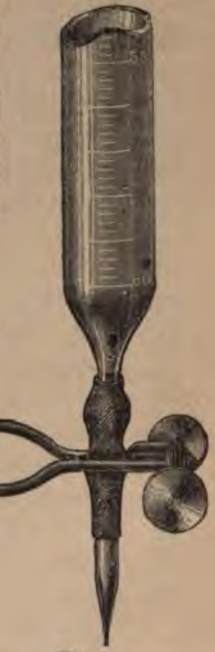

FIG. 2.

By pressing this part of the tube between the thumb and forefinger, a channel may be made along the side of the rod, which may be regulated at will, so as to deliver the fluid in a stream or in drops. The only objection to this form of burette is that it cannot be used with potassium permanganate solution, which acts upon the rubber. A number of modifications have been proposed to avoid this difficulty, but the best way out of it is to purchase a burette with glass

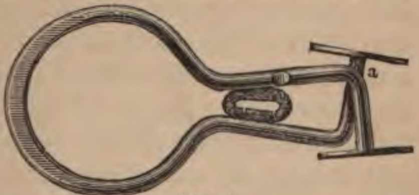

FIG. 3.

cock to be used for that solution alone. Another form of burette valve is that of Prof. Koenig, of the University of Pennsylvania. This is shown in Fig. 5, and is easily understood. The plate, which closes the capillary orifice, is covered with a small piece of india-rubber cemented to the spring by means of a solution of rubber in chloroform. The spring itself is also dipped several times in the rubber solution, and, as the chloroform evaporates, a thin film is left protecting it from the action of acids. These burettes may be used with any solution, do not leak, and the rubber is not sensibly attacked. Iodine solution, however, must not be allowed to remain in the burette any great length of time, as the German-silver spring is attacked by it. Still another form of valve which is intended to replace a glass stopcock is shown in Fig. 6.* It has two principal objections: the first, that it is difficult to make a perfectly tight joint, and the second, that small particles suspended in the liquid are apt to get in the joint and cause leakage.

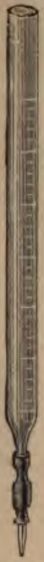
FIG. 4.

Gay-Lussac's burette, shown in Fig. 7, has several disadvantages, among which are that it is very fragile and easily broken; that it must be held in the hand, which communicates its heat to the contents and so slightly increases the volume of contained fluid, and that it is difficult to regulate the flow with exactness. Mohr has modified this burette so as to remedy these points by placing it on a wooden foot and closing at the top by a perforated cork with a tube inserted, by blowing into which the flow may be very accurately regulated. His arrangement is shown in Fig. 8. Geissler's burette is like Gay-Lussac's, except that the small tube is placed inside the large one. Casamajor's burette*, shown in Fig. 9, has the advantages of portability and being easily handled without heating the fluid. By inclining the burette, grasping it at the top, and turning the tube, the flow may be regulated at will. Mohr's burette, when it can be used, is to be preferred to any of the forms above described, and, with potassium permanganate, it is preferable, as before stated, to have a burette with glass stop-cock. This stop-cock should have the shape shown in Fig. 10, and must be accurately ground. Before being used, the tap should be removed and *slightly* greased with clean tallow. This causes it to turn easily in the socket, and makes the joint perfectly tight. Burettes with glass cock may be used with any solutions except caustic alkalies, which are apt to attack the glass at the cock, and cause it to stick. With Mohr's burette, the pinch-cock (Fig. 3) may be used, or either of the forms shown in Fig. 11; the one shown in Fig. 3 is, however, to be preferred. The metal disks of this clamp are soldered to the wires, which has been alleged as an objection to its use, as acid attacks

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* Britton, American Chemist, vol. vii., p. 50.

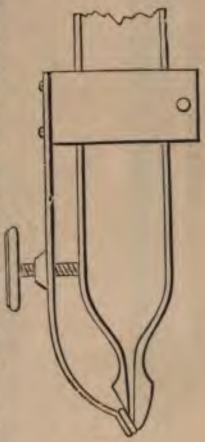

FIG. 5.

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* American Chemist, vol. vii., p. 213.

the solder and causes the disks to fall off, but the first cost of the instrument is small, and it can be replaced as often as necessary. It is certainly a much more convenient form than any of the substitutes which have been proposed. For the purpose of filling the burette rapidly, where many successive analyses of the same kind are to be made, Mohr places a **T**-shaped glass tube between the burette and the pinch-cock, and the third arm of this is connected with the bottle containing the standard solution, by a piece of rubber tubing, as shown in Fig. 12. By pressing on the pinch-cock, shown at the right in the figure, the solution flows into the burette, and may be immediately used for titrating. When a burette is filled with liquid, it will be noticed that the surface has the appearance shown in Fig. 13. This is due to the capillary attraction which the glass exerts toward the water.

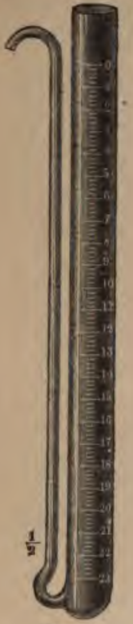

FIG. 7.

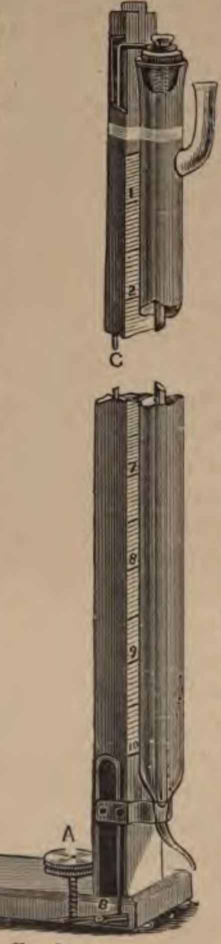

FIG. 6.

It is an important point, in reading, to select one of these surfaces, and to use that invariably in estimating the amount of fluid. The point generally taken is the lower surface of the meniscus, and all large pieces of apparatus, such as flasks, mixing cylinders, etc., are graduated in that way. For reading burettes, Mohr uses a small card, the upper part of which is white, while the lower half is blackened. By placing this on the side of the burette opposite the eye, so that the dividing line between the black and white portions is 2 to 3 mm. below the lower surface of the liquid, and bringing the eye on a level with it, the lower portion of the meniscus is bounded by a sharply defined black line, by which it may be very accurately read. A better plan is to make use of the float invented by Erdmann,* shown in Fig. 14. It is a piece of thin glass tubing, with a small bulb at the lower end contain-

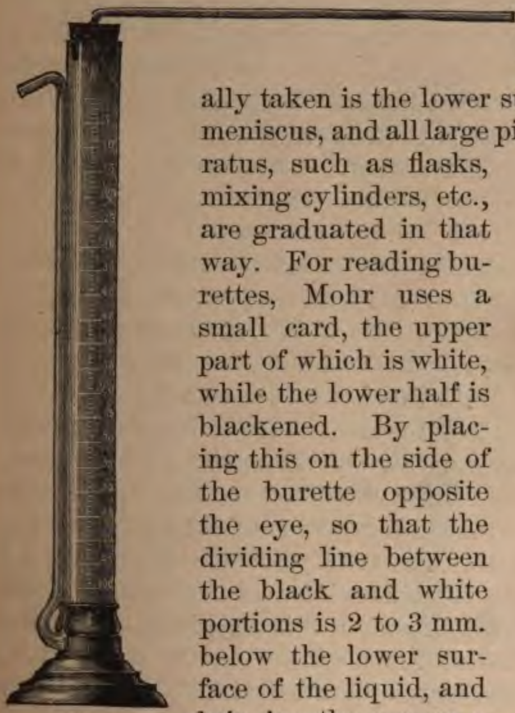

FIG. 8.

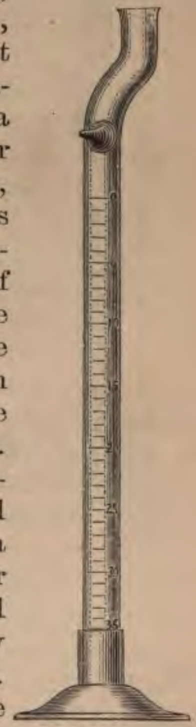

FIG. 9.

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* Liebig's Annalen, 103, 359.

ing mercury, to keep it in an upright position, and drawn out at the top into a small ring, by which it may be easily lifted from the burette. A line is engraved entirely around the float, and the amount of mercury placed in the bulb is so regulated that it will just float in water. To read the burette, the eye is so placed that the lines behind and in front coincide, and the corresponding point on the burette noted. The float should be slightly smaller than the interior of the burette, so that it may move up and down with ease; but it should not have too much play, or it will show an inclination to adhere to the walls and produce incorrect readings. Each burette in use should have a swimmer of its own. When the mercury used to weight the swimmer is allowed access to the upper bulb, it is slowly oxidized and covers the interior with a yellowish coating, through which it is difficult to see the line at the back. To remedy this, the mercury is placed in the small bulb below and sealed in, either by fusing a small bit of sealing-wax in the opening or by sealing it in a blow-pipe flame.*

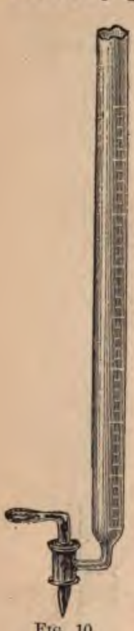

FIG. 10.

Burettes are made from tubes of nearly uniform width. They are filled with liquid to the mark made at the 0 point, and then 30, 50, or 100 c. c. run out and another mark made. After this, they are placed in a dividing engine, and the distance between the two points divided in 30, 50, or 100 equal parts, and these subdivided into fifths or tenths. These

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* Volhard, Liebig's Annalen, 176, 240.

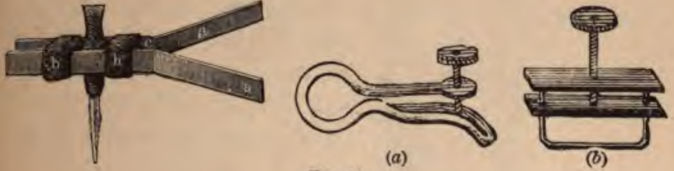
(a) (b)

Fig. 11.

divisions are then either ground or etched on the glass. Inasmuch as it is very rarely possible to obtain tubes of exactly the same dimensions throughout, these divisions do not always represent exact cubic centimetres and parts of cubic centimetres as they pretend to do. If, for example, the tube of the burette is widest in the upper part, the divisions there will contain more than those lower down. Before using a new burette, it is therefore absolutely essential that this error, if any, be determined. To do this, fill the burette to the 0 mark with distilled water at the temperature of 16° and run out 10 c. c. into a small

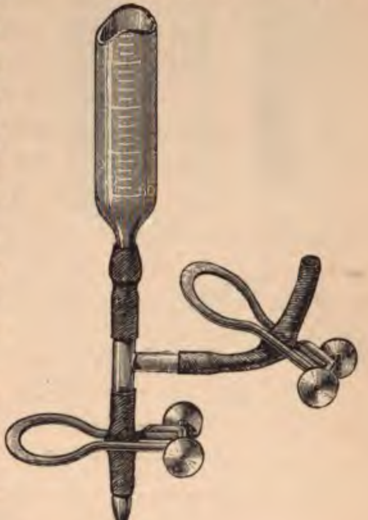
Fig. 12.

weighed flask and weigh it again, then run in a second 10 c. c. and weigh; repeating this until the burette is empty. By subtracting the 1st weight from the 2d, the 2d from the 3d, etc., it is easy to find how much each 10 c. c. of water weighed; and as each should weigh exactly 10 gms., the error, if any exists, is at once apparent. Small errors up to 5 to 10 milligrammes in 10 c. c. may be entirely neglected. The following weighings were made in ascertaining the error of graduation of a burette used by the author.

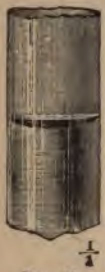

FIG. 13.

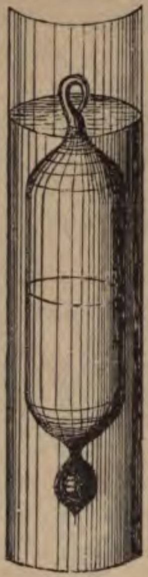

FIG. 14.

Correction for burette marked *a*,

Flask		weighed	20·0052.
"	+ 10 c. c.	"	30·1059.
"	+ 20 c. c.	"	40·1548.
"	+ 30 c. c.	"	50·1346.
"	+ 40 c. c.	"	60·0712.
"	+ 50 c. c.	"	70·0202.

1st	10 c. c.	weighed	10·1007.
2d	10 c. c.	"	10·0489.
3d	10 c. c.	"	9·9798.
4th	10 c. c.	"	9·9366.
5th	10 c. c.	"	9·9490.

The following table was constructed from these data:

Apparent No. of c. c.	Real No. of c. c.	Apparent No. of c. c.	Real No. of c. c.	Apparent No. of c. c.	Real No. of c. c.
1	1·01	18	18·14	35	35·1
2	2·02	19	19·14	36	36·09
3	3·03	20	20·15	37	37·08
4	4·04	21	21·15	38	38·08
5	5·05	22	22·15	39	39·07
6	6·06	23	23·14	40	40·07
7	7·07	24	24·14	41	41·06
8	8·08	25	25·14	42	42·06
9	9·09	26	26·14	43	43·05
10	10·1	27	27·13	44	44·05
11	11·1	28	28·13	45	45·04
12	12·11	29	29·13	46	46·03
13	13·12	30	30·13	47	47·03
14	14·12	31	31·12	48	48·03
15	15·12	32	32·12	49	49·02
16	16·13	33	33·11	50	50·02
17	17·13	34	34·10		

It is best to prepare such a table in all cases where the burette is incorrect, and to fasten it in the note-book or upon the wall of the laboratory for convenience of reference.

It will be noticed that in the above table the calculation is not carried further than the second decimal place, and this is entirely unnecessary, since even with Erdmann's swimmer we are not able to read closer than ·025 c. c.

Burettes are intended to *deliver* given volumes of fluid, and will *contain* a little more than the graduation indicates.

Stands for supporting burettes are made of various forms. One of the best of these is shown in Fig. 15. It is capable of holding several burettes, and may also be used for supporting pipettes. A form given by Fresenius is shown in Fig. 16. It is intended for two burettes. The simplest, cheapest, and best form of stand that has come under my notice is that shown in Fig. 17, for which we are indebted to Prof. Wing, of Boston. It is intended to support two burettes, only one of which is shown in the figure. The burette is secured by two strings passed over it and fastened by turning pegs to which the strings are attached. Fig. 18 is the form which will be found most convenient where only one burette is in use.*

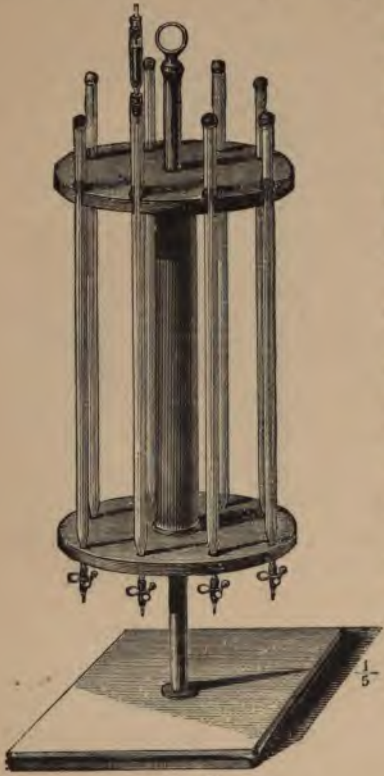

FIG. 15.

PIPETTES.

Pipettes are of two kinds—those which are graduated like burettes, and those which are intended to deliver only one determinate portion of liquid, and have therefore only a single mark or graduation. Those of the first kind are simply burettes contracted at the top to admit of regulating the flow of liquid by the finger. Only the smaller sizes of these, below 5 c. c., are much used. The larger sizes are sometimes used for estimating roughly the strength of solutions previous to a more careful determination with the burette.

---

* To prevent evaporation, it is best to place a marble upon the burette while in use, which shuts out dust as well, or, better, slip an inverted test-tube over it.

Pipettes of the second class, or volume pipettes, are used for dividing solutions and for measuring out portions of fluids with exactness. They are made of the following sizes: 1, 2, 5, 10, 20, 25, 50, 100, and 150 c. c.

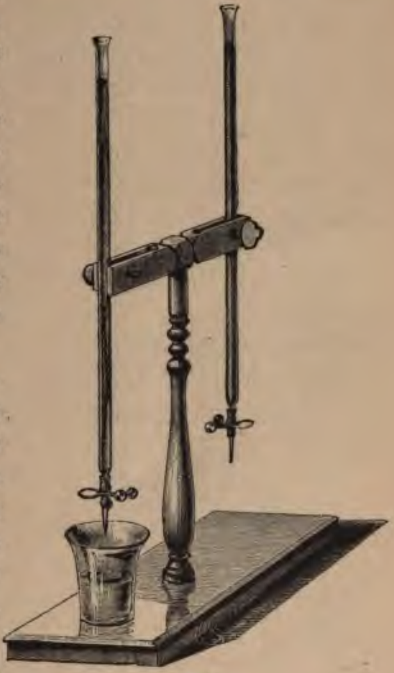

FIG. 16.

Up to 20 c. c. they may have the shape of Fig. 19. The larger sizes should have the shape of Fig. 20.

The external diameter of the small sizes must not be greater than 15 mm. in the larger part of the tube, otherwise they cannot be inserted in the necks of small flasks. The internal diameter of the small tube upon which the graduation is made should not be greater than 5 mm. In the 25 c. c. pipettes, the lower small tube should be at least 20 centimetres long, and proportionately longer in the larger sizes. It is better in all cases that the graduation-mark should be placed near the lower portion of the small tube, to which suction is applied, as the fluid is apt to be sucked into the mouth if this lies higher up.

There are three different methods of delivering the fluid from pipettes:

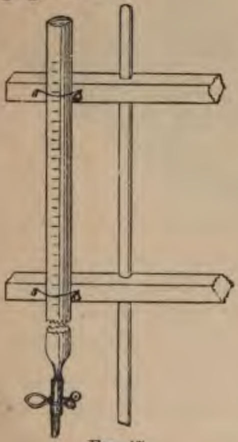

FIG. 17.

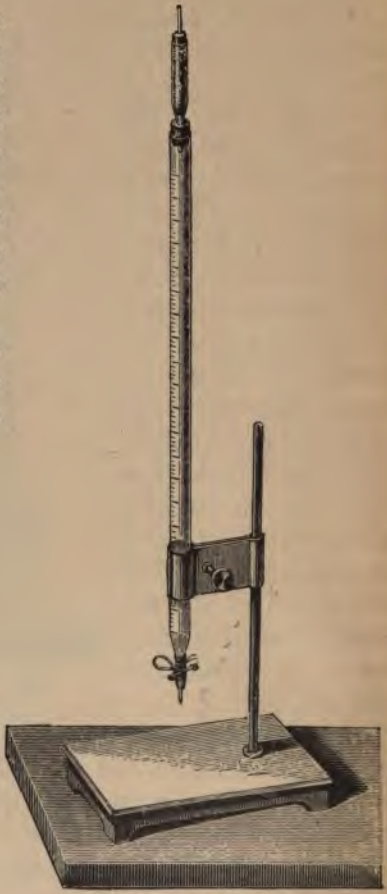

FIG. 18.

First, by simply allowing it to run out without assistance, in which case one or two drops remain in the lower portion of the delivery tube.

Second, by allowing the fluid to run out, and then blowing out the drops adhering to the point with the aid of the breath.

Third, by placing the point of the burette slightly inclined against the side of the vessel, and allowing the fluid to run out in that way.

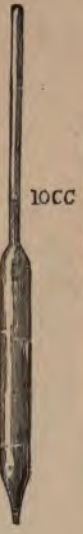

FIG. 19.

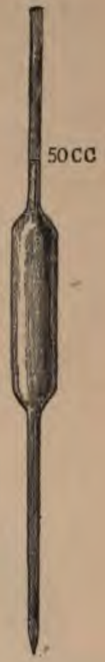

FIG. 20.

The third method is to be preferred, and is the one generally adopted. The flow of the fluid is somewhat hastened, and the portion which remains adhering to the point has nearly the same volume in successive operations. Whichever method is adopted, it should be rigidly adhered to throughout. Pipettes, like burettes, are graduated to deliver.. To test their accuracy, it is sufficient to fill to the mark with distilled water at 16°, empty into a flask which has been previously weighed, and weigh this a second time. The difference of the two weights in grammes should be the number of c. c. contained by the pipette. Differences of 5 to 10 mgs. may be disregarded. When the graduation is incorrect, a new one may be made by filling the pipette with distilled water, allowing it to run out, closing the point by a small bit of wax, and running in from the burette the required number of c. c. The new mark may be made with a sharp file dipped in turpentine, to prevent subsequent breaking of the glass.

MEASURING-FLASKS.

These are used for preparing standard solutions; dividing solutions with the aid of the pipette, etc. They are of the following capacities: 100, 200, 250, 300, 500, and 1000 c. c. graduated to *contain*. It is also convenient to have 100 and 200 c. c. flasks graduated to *deliver*. Sometimes the same flask has two graduations: one to contain, the other to deliver. They should be tolerably long in the neck, which should have an internal diameter of about 20 mm. The graduation-mark should be a little below the

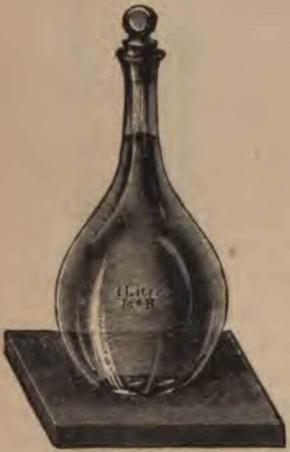

FIG. 21.

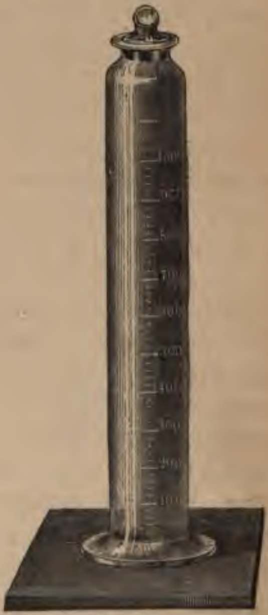

FIG. 22.

middle of the neck. They must be fitted with accurately ground stoppers to admit of shaking fluids contained in them.

Mixing cylinders (Fig. 22) are convenient for rough measurement of fluids, etc. They are also fitted with well-ground stoppers.

It is most convenient to test the accuracy of the graduation of flasks by the aid of a balance capable of carrying 2 kilogrammes and turning with 5 milligrammes. The perfectly clean and dry flask is to be counterpoised, and then filled to the mark with distilled water of 16°, when the increase in weight should be exactly 1 kilogramme with the litre, 500 gms. with the 500 c. c. flask, etc.

VOLUMETRIC ANALYSIS WITHOUT A BURETTE.

Instead of measuring the volume of a standard solution, we may weigh it; and as the weight is independent of temperature, this method is often resorted to where great accuracy is desired. It is a slower process, however, and on this account less frequently used.

The standard solution is placed in the little flask, Fig. 23, and the whole weighed on a balance capable of turning with ·02 gms. The solution is then run into the beaker containing the substance to be estimated, and, after sufficient has been added, again weighed. The difference in weight is the amount of solution used. If the standard solution is used in this way, it must of course be standardized in the same manner.

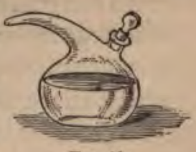

FIG. 23.

VOLUMETRIC ANALYSIS WITHOUT WEIGHTS AND WITHOUT STANDARD SOLUTIONS.

The way in which this is performed can be best explained by an example. Suppose we have an iron ore whose percentage in iron we wish to determine. The ore is pulverized, and a portion of it placed upon one pan of a balance. Pieces of pure iron wire are then placed upon the opposite pan until equilibrium is attained. Both are dissolved in acid, the ore solution treated with zinc to reduce the iron to the ferrous state, and then both solutions titrated with a solution of permanganate of unknown strength. The iron requires 20 c. c. and the ore 11·5 c. c. Then $20:11\cdot5::100:x$. $x = 57\cdot5$, which is the percentage of iron contained in the ore. In the same way, various other estimations may be performed, as soda ash by weighing against pure sodium carbonate, crude oxalic acid by weighing against the pure article, etc.

VOLUMETRIC ANALYSIS WITHOUT BALANCE OR WEIGHTS.

This can only be performed where but two substances are present in the body to be analyzed, which can be separated, and estimated by the same solution. Brass, for instance, contains only copper and zinc. A small piece is dissolved in acid, and the copper precipitated by H_2S, filtered off, dissolved in nitric acid, ammonia added in excess, and the copper precipitated by a solution of sodium sulphide of unknown strength. The solution which contains the zinc is then made ammoniacal, and the zinc precipitated by the same solution of sodium sulphide. The c. c. of sodium sulphide used for the copper are then multiplied by the atomic weight of copper, and the c. c. used for the zinc by the atomic weight of zinc. Numbers are obtained in this way which express the proportion of the metals to each other, and from these the percentage can be calculated. Suppose in an alloy known to contain only copper and zinc, a small piece was treated in this way, and for the copper 25 c. c., for the zinc 20 c. c. sodium sulphide were used. Then, copper : zinc : : $25 \times 63{\cdot}36 : 20 \times 65{\cdot}16$; copper : zinc : : 158400 : 130320; consequently the copper forms $\frac{158400}{288720}$ of the alloy, or 54·87 per cent, and the zinc $\frac{130320}{288720}$, or 45·13 per cent.

ON THE SOURCES OF ERROR IN VOLUMETRIC PROCESSES.

The volumetric process is liable to certain sources of error, in addition to those of the gravimetric method.

1. A small excess of the standard solution must generally be added to show the completion of the reaction, and this small excess, unless a correction be applied, is counted as performing part of the work. In many cases, this error is extremely small, on account of the delicacy with which an excess is shown. When the analysis must be made with great accuracy, or where the end of the reaction is not shown very sharply, a correction may be applied as follows: Take a quantity of water in a beaker, and, by the proper reagents, give it the color which

the solution is to have at the completion of the analysis; then add the substance to be analyzed, and run in the standard solution until the same color makes its appearance. As an example, suppose it be required to make an analysis of a solution of sulphydric acid with great accuracy. We take a large beaker containing water, and add some ammonium carbonate, then enough iodine and starch solutions to give it a faint blue color. Then a measured or weighed amount of the H_2S solution is poured in, and standard iodine solution run in from a burette until the same color is again produced. In some cases, the solution of the substance to be analyzed is very dilute, and we must then make the correction in the following way: First, add the standard solution to the substance to be analyzed until the appearance which marks the end of the reaction is produced; then with the same standard solution, and an indicator if necessary, produce the same appearance in a like volume of pure water, and subtract the c. c. of standard solution used for the water from the c. c. used for the actual analysis, the remaining c. c. will be the amount which took part in the reaction.

2. If the fluid in a burette or pipette be run out, at one time rapidly, at another slowly, different amounts of fluid will be obtained. It is therefore necessary always to deliver burettes or pipettes with the same rapidity. This precaution is especially necessary with burettes, as the delivery of a pipette is regulated by the size of the opening at the point. The best practice is to deliver the fluid slowly, as more constant results are obtained in this way. The burette and pipette must be kept scrupulously

clean, and should be rinsed from time to time, first with a solution of caustic potassa, then with nitric acid, and finally with distilled water.

The solutions which are divided by means of pipettes should be dilute, since concentrated salt solutions adhere to glass with different degrees of tenacity. Tatlock* found that a pipette delivering 1000 grains of water at 60° F. delivered the following amounts of different salt solutions:

	SP. GR.	GRS. DELIVERED.
$(NH_4)_2SO_4$	1·2500	997·6
KCl	1·1812	998·4
$NaCl$	1·2072	997·7
$ZnSO_4$	1·4264	995·2
NH_4Cl	1·0724	999·5

Temperature also has some influence upon the adherence of solutions to glass, it being greater at low and less at high temperatures.

3. Influence of temperature.

The volume of all liquids is affected by a change of temperature, and this is true of the solutions which are employed in volumetric analysis. As the solutions used consist principally of water holding small quantities of other substances dissolved, they are generally regarded, so far as expansion and contraction are concerned, as pure water and the coefficient of expansion, of pure water used for finding the correction to be applied. Unfortunately, however, standard solutions do not expand like pure water, some of them departing widely from it, and nearly all of them expand more rapidly. All methods of correcting the volume of a solution for the temperature by the expansion coefficient of water, therefore, are insufficient.* The only proper method is to standardize solutions at the temperatures at which they are to be used, and then no correction need be applied. In general, however, the temperature of a laboratory does not vary to any very considerable extent, and it is usually safe, if the solutions are all made and standardized at one temperature, to neglect the small error due to expansion entirely. The temperature at which standard solutions are made, and flasks, pipettes, and burettes graduated, varies. In this country, 15° C. and 60° F. are often used. Mohr uses 17·5°, Sutton 16°, and Fresenius takes as the standard of volume the litre of water weighing 1000 grms. at 4°, or 999·981 at 16°. No advantage is obtained by this last method, and the litre is best taken as 1000 grms. pure water weighed in air, with brass weights, at 16° centigrade, and 760 mm. barometer. Practically, it makes no difference whether the solution be made at 15°, 16°, or 17·5°, since the change in volume between these limits cannot be detected by ordinary volumetric apparatus.

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* Chemical News, xxiii., 13.

PREPARATION OF SOLUTIONS.

WHEN much volumetric work is done, it is very convenient to have the solutions used in titrating equivalent to one another in strength; 1 c. c. of silver solution, for instance, should contain enough silver to exactly precipitate the chlorine contained in 1 c. c. of standard hydrochloric acid, sodium chloride, or barium chloride. The barium chloride solution, in turn, should precipitate the sulphuric acid from an equal volume of standard sulphuric acid solution, etc.

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* See Casamajor, American Chemist, vol. vii., p. 249.

This is easily accomplished if we weigh out in each case the hydrogen equivalent of the reagent in grammes, dissolve in water, and dilute to 1000 c. c.

In the case of univalent substances, the atomic or molecular weight in grammes is the proper amount to be taken; for example, hydrochloric acid = 36·457 gms. per litre, sodium chloride = 58·5 gms. per litre, and iodine = 126·85 gms. per litre.

With bivalent substances, one half the atomic or molecular weight is taken; for example, sulphuric acid $= \frac{98}{2} = 49\cdot$ gms. per litre, sodium carbonate $= \frac{83\cdot043}{2} = 41\cdot521$ gms. per litre.

With trivalent substances, one third of the atomic weight is taken, etc.

In every case, however, attention must be paid to the reaction to be accomplished, as this determines the valence of the substance, and therefore the amount which must be used. Potassium bichromate, for example, when used as an oxidizing agent, gives up 3 atoms of oxygen, and has therefore in this case a valence of 6 and $\frac{1}{6}$ the molecular weight, or 49·179 gms. are used per litre. When used for precipitating, however, it throws down but 4 equivalents of a univalent metal, and $\frac{1}{4}$ the molecular weight, or 73·7685 gms., is the amount necessary.

Solutions made as above are called normal solutions. In many cases, they are too strong and are diluted 10 or 100 times, and are called deci- and centi-normal, written $\frac{n}{10}$, $\frac{n}{100}$.

If we take $\frac{1}{10}$ equivalent weight in grammes of a substance for analysis, using normal solutions, or $\frac{1}{100}$, using $\frac{n}{10}$ solutions, the number of c. c. used will express also the percentage of pure substance sought for, which the sample contains.

Suppose, for example, we take a piece of iron wire weighing ·56 gms., or $\frac{1}{100}$ eq., and use 99·7 c. c. $\frac{n}{10}$ permanganate. The wire contains therefore 99·7 per cent pure iron.

This fact is often taken advantage of in technical work where a great number of analyses are made, as by it much calculation is saved.

In the preparation of standard solutions, it must be borne in mind that most salts, when dissolved in water, cause a falling in the temperature. Other substances—as, for example, sulphuric acid and sodium hydrate—cause a rise in the temperature. In either case, the solution should be allowed time for attaining the temperature of the air before being measured. Most salts, concentrated sulphuric acid, strong saline solutions, etc., cause a condensation in volume when dissolved in water, and this fact must also be borne in mind. In making normal solutions, it is sometimes best to weigh out a little more than the amount required by theory; dissolve and dilute to 500 c. c.; then determine the strength very carefully, and measure into the litre flask as much of this solution as will produce the proper strength when diluted to 1 litre. In all cases, after the solution has been diluted to the litre, and is supposed to be of normal strength, it should be very carefully titrated against the proper substance and proved normal before being used.

For a method of making up large quantities of normal solution rapidly, see "Chemical News," xxvi., 159, and xxix., 23.

It is not always convenient to prepare solutions of exactly normal or decinormal strength, as this sometimes, especially when large quantities of solutions are made, becomes a very tedious process. It is usual then to make the solution approximately normal, and find its precise strength. Then a factor is found, multiplying by which brings the number of c. c. to what it would be were the solution strictly normal. For example, the strength of an approximately normal solution of sodium hydrate is found as follows: ·63 gms. oxalic acid dissolved in water and titrated, require 10·5 c. c. soda solution. If the solution of sodium hydrate were normal, only 10 c. c. would be required; it is, therefore, too weak, and more is used for an analysis than would be done were the acid of normal strength, and the number of c. c. used for an analysis must in each case be multiplied by $\frac{10\cdot}{10\cdot5}$, or ·952381. The bottle containing the solution should have the proper factor marked on the label. In this case, it would be, sodium hydrate × ·952381 = normal. It sometimes happens that two solutions of the same substance are at hand, one stronger and the other weaker than the normal standard. In this case, by determining the exact strength of each and mixing them in the proper proportions, the normal strength may be obtained without further trouble. Suppose, for example, we have two solutions of sodium hydrate, which, by titration, we find to be of such a strength that 10 c. c. normal oxalic acid = 5 c. c. of the stronger and 10 c. c. normal oxalic acid = 15·5 c. c. of the weaker. Let the volume of the stronger solution, which is required to saturate 10 c. c. of normal acid, be represented by *a*, and the volume of the weaker acid by *b*. Then let the proportions in which they are to be mixed to form a normal solution be represented by *x* and *y* respectively. A volume of the stronger solution will saturate 10 c. c. normal acid $\frac{10\,x}{a}$ times, and a volume of the weaker solution $\frac{10\,y}{b}$ times; both together saturate $\frac{10\,x}{a} + \frac{10\,y}{b} = x + y$.

Clearing of fractions $10\,bx + 10\,ay = abx + aby$; transposing

$$10\,bx - abx = aby - 10\,ay$$
$$bx\,(10 - a) = ay\,(b - 10);$$

dividing by $by\,(10 - a)$,

$$\frac{x}{y} = \frac{ay\,(b - 10)}{by\,(10 - a)}, \text{ or } \frac{x}{y} = \frac{a\,(b - 10)}{b\,(10 - a)}$$
$$x : y :: a\,(b - 10) : b\,(10 - a).$$

Substituting the values of *a* and *b* in the above example, we have

$$x : y :: 5\,(15{\cdot}5 - 10) : 15{\cdot}5\,(10 - 5), \text{ or}$$
$$x : y :: 27{\cdot}5 : 77{\cdot}5.$$

GENERAL METHODS.

As was explained on page 2, all the reactions used in volumetric estimations may be classed under three heads:

1. Saturation.
2. Oxidation or Reduction.
3. Precipitation.

ANALYSIS BY SATURATION.

SOLUTIONS REQUIRED.—SODIUM CARBONATE.

Normal Solution = 53·043 gms. Na_2CO_3 per litre.

A somewhat larger quantity than 53 gms. pure effloresced sodium carbonate is heated to dull redness (not to fusion), allowed to cool under the desiccator, and exactly 53·043 gms. weighed out. As the sodium carbonate absorbs moisture slowly during the weighing, this must be done quickly. It is then dissolved in water, and the solution diluted to one litre. If pure carbonate cannot be had, it is easy to prepare it by passing a stream of washed CO_2 through a saturated solution of the purest sodium carbonate that can be obtained. The resulting precipitate is to be drained from the adhering mother liquor by means of the Bunsen filter pump, and afterward by pressure between filtering paper. Eighty-five gms. of the hydrogen sodium carbonate so obtained, when ignited to dull redness for about ten minutes, leave 53·6 gms. Na_2CO_3, or slightly more than the proper amount. $2(NaHCO_3) = Na_2CO_3 + H_2O + CO_2$.) Mohr ascertains the correctness of the standard solution by evaporating 50 c. c. to dryness in a small platinum dish, drying perfectly, and heating over the lamp until the bottom of the dish is of a very dull red. The dish is allowed to cool under the desiccator, and then quickly weighed. The sodium carbonate so obtained should weigh 2·65 gms. It is also advisable to compare its strength with that of the standard acids.

OXALIC ACID.

Normal Solution = 63 gms. $C_2H_2O_4+2H_2O$ per litre.

Commercial oxalic acid generally contains calcium oxalate and acid potassium oxalate, from which it must be purified before being used. The purest acid which can be obtained is to be tested for lime and potassium by vaporizing a portion over the lamp in a platinum crucible, and examining the residue, if any remains, for these two substances. If the acid contains calcium oxalate, it may be purified by adding a quantity of lukewarm water insufficient to dissolve all the crystals, and filtering off the portion dissolved. The lime remains behind. The solution is then evaporated until a portion of it crystallizes out. This first portion contains most of the foreign salts, including the acid potassium oxalate, if any be present. These crystals are rejected, the mother liquor is evaporated, and the crystals obtained from this, after one or two recrystallizations, will be pure oxalic acid. They must volatilize completely, leaving no residue whatever. They are to be dried by pressure between filtering paper, and afterward allowed to lie in a cool place, exposed to the air, but protected against dust until all hygroscopic water has evaporated. Sixty-three gms. of the dry acid are to be dissolved in distilled water, washed into the litre flask, and the flask filled to the containing mark with distilled water of 16°. This solution is apt to decompose slightly unless protected from the action of light. For this purpose, the bottle containing it should be slipped into a bag made of black material, and this tied tightly around the neck of the bottle. The normal solution sometimes deposits crystals when exposed to low temperatures, and should therefore always be shaken before being used.

Before being employed, the solution must be titrated against the sodium carbonate solution, and also against the $\frac{n}{10}$ potassium permanganate solution.

One c. c. should be equal to 1 c. c. normal sodium carbonate, and 10 c. c. $\frac{n}{10}$ potassium permanganate.

SULPHURIC ACID, H_2SO_4.

Normal Solution = ·49 gms. H_2SO_4 per litre.

Add 30 c. c. of the concentrated acid to half a litre of water, and allow the mixture to stand until the temperature of 16° is reached. Two separate portions of this dilute acid, of 10 c. c. each, are then to be measured off, and the exact amount of sulphuric acid in the first found by titrating against sodium carbonate (see page 38). In the second, it is to be precipitated by $BaCl_2$, and the amount of H_2SO_4, calculated from the weight of $BaSO_4$, found. Having found the exact amount of H_2SO_4 contained in 1 c. c. of the dilute acid, the number of c. c. to be introduced in the litre flask, so as to give the proper strength on dilution, may be calculated from the following formula:

$$\text{Number of c. c. to be used} = \frac{49}{\text{gms. } H_2SO_4 \text{ in 1 c. c.}}$$

If, for example, 1 c. c. of an acid prepared as above be found to contain ·135 gms. H_2SO_4 in 1 c. c., then

$$\text{Number of c. c. to be used} = \frac{49\cdot}{\cdot 135} = 362\cdot 96 \text{ c. c.}$$

This amount must then be measured into the litre flask, and the flask filled to the mark with water of 16°.

HYDROCHLORIC ACID, HCl.

Normal Solution = 36·457 gms. HCl per litre.

The strongest hydrochloric acid of commerce contains 42·43 per cent HCl gas, and has a specific gravity of 1·21. Roscoe and Dittmar have shown that when a solution containing HCl is distilled at the ordinary pressure a liquid containing 20·22 per cent HCl, and having a sp. gr. of 1·1, finally distils over. If the solution be stronger, in the first place, gas is given off until this composition is reached, when the solution distils over unchanged. If the acid be originally weaker, water distils over at first. About 75 c. c. of the acid of 1·21 sp. gr., or 170 c. c. of the acid of 1·1 sp. gr., are to be diluted to 500 c. c., and two portions, of 10 c. c. each, are taken out, in one of which the strength is estimated by means of the sodium carbonate solution, and in the second by precipitation with silver nitrate and weighing the silver chloride obtained. The exact strength of this solution being known, the proper amount is introduced into the litre flask, and the flask filled to the mark with water. A solution of this strength may be boiled without losing acid, and it is in many cases a far better solvent than either standard nitric or sulphuric acid.

NITRIC ACID, HNO_3.

Normal Solution = 63·044 gms. HNO_3 per litre.

About 105 gms. of the dilute acid sp. gr. 1·3 are diluted to 500 c. c., and two portions, of 10 c. c. each, are taken out. One of these is titrated with standard sodium carbonate; the other is to be placed in a platinum evaporating dish, an excess of pure ammonium hydrate added, the solution evaporated to dryness, and heated in the air-bath at 110° to 120°. The residue will be ammonium nitrate, from the weight of which the nitric acid may be calculated. After the strength is known, place the proper amount in the flask and dilute to the litre.

SODIUM HYDRATE, NaOH.

Normal Solution = 40·043 gms. NaOH per litre.

About 90 gms. of the purest sodium hydrate that can be obtained may be dissolved in water and diluted to 500 c. c. The strength of the solution is best estimated by titration against a weighed amount of pure oxalic acid. After the exact strength has been found, the proper amount is to be measured into the litre flask and diluted to a litre. The solution must be free from carbonic acid, and should be kept in a bottle like Fig. 24. The tube is filled with a mixture of sodium sulphate and lime, which has been ignited and broken into small pieces. This absorbs all carbonic acid and prevents any from entering the bottle. If pure sodium hydrate cannot be bought, it may be made by boiling a solution of one part sodium carbonate ($Na_2CO_3 + 10H_2O$) in ten parts water with one part lime, previously slaked and made into a thin cream with water. The operation is conducted in a silver basin or clean iron pot. After boiling the mixture for half an hour, replacing the water as fast as it evaporates, cover the vessel and allow it to cool. The calcium carbonate, together

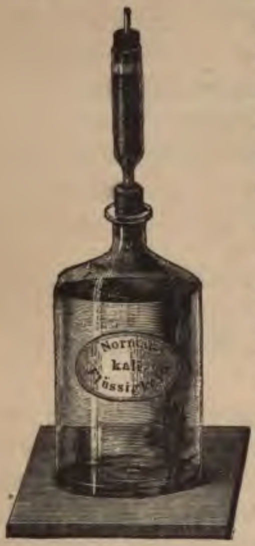

FIG. 24.

with the excess of lime, settles to the bottom, and the clear solution of sodium hydrate may be decanted and diluted to the proper strength.

POTASSIUM HYDRATE, KOH.

Normal Solution = 56·137 gms. KOH per litre.

Prepared and preserved like sodium hydrate. It is to be preferred to the latter, because it does not attack glass vessels quite as strongly.

AMMONIUM HYDRATE, NH_4OH.

Normal Solution = 35 gms. NH_4OH, or 17 gms. NH_3 per litre.

The solution of ammonium hydrate of sp. gr. ·88 may be used. It must be perfectly free from carbonic acid, and must leave no residue when evaporated to dryness. About 60 c. c. are to be diluted to a half litre, two portions of 10 c. c. each rapidly measured out and titrated, one against standard oxalic, and the second against standard hydrochloric or sulphuric acid. After ascertaining the exact strength, measure the proper amount into the litre flask and dilute. All these operations are to be performed as rapidly as possible, as there is danger of the solution of ammonia losing strength if allowed to stand exposed to the air. In order to preserve the solution from the carbonic acid in the air, it must be kept in a bottle provided with a tube containing a mixture of ignited sodium sulphate and lime. This solution is apt to lose ammonia in very small quantity when poured from the bottle into the burette, and the arrangement shown in Fig. 25 is preferable when using it. The bottle and burette should both be provided with tubes for absorbing CO_2.

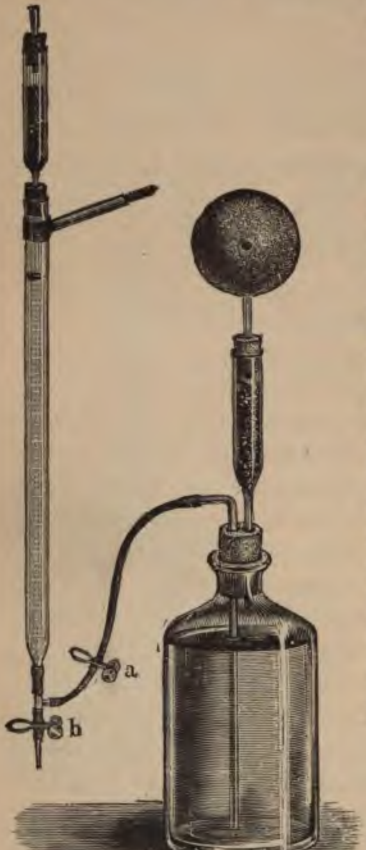

Fig. 25.

INDICATORS.

Indicators are substances added to show when the reaction is completed. In analysis by saturation, it is necessary to add a solution of some coloring matter which is changed in color by an excess of the titrating fluid. Litmus is mostly employed, and, in spite of the many objections that have been made to it, and the infinite number of substitutes proposed, still remains in general use.

Litmus.

Sutton gives the following directions for the preparation of litmus solution:

"Boil the litmus, previously reduced to coarse powder, two or three times with alcohol of about 80 per cent, and throw the liquid so obtained away. (This treatment removes some coloring matter which is a hindrance to the proper reaction.) Then digest the litmus repeatedly with cold distilled water till all soluble color is extracted, let the mixed washings settle clear, decant and add to them a few drops of concentrated sulphuric acid until quite red, then heat to boiling; this will decompose the alkaline carbonates and convert them into sulphates. Now cautiously add baryta water until the color is restored to blue or violet, let the baric sulphate settle perfectly, and decant into a proper vessel for use."

Solution of litmus must be kept in an open bottle. If the bottle is stoppered, the solution gradually loses color. Upon again exposing to the air, however, the color is entirely restored. A single drop of dilute acid should change the color of a large quantity of such a solution to a deep red. With carbonic acid litmus is slightly reddened, and it is for this reason difficult to say, in a solution containing carbonic acid, whether other free acid is present, unless the carbonic acid be first expelled by boiling. Boracic acid behaves like carbonic.

Cochineal Solution

Is frequently used in acidimetry and alkalimetry, and possesses the advantage that carbonic acid affects it less than litmus. About 3 gms. cochineal are digested in a mixture of 40 c. c. alcohol and 160 c. c. water.

THE ANALYTICAL PROCESS.

If an acid is to be estimated, a portion is weighed or measured into a beaker, diluted with water, and sufficient litmus added to color it strongly red. Standard sodium, potassium, or ammonium hydrate is then run in from a burette until the color of the litmus changes to blue. The change of color in this case is very sharp, and the exact point is easy to hit.

If an alkali is to be estimated, we proceed in the same way, using standard acid (either oxalic, sulphuric, nitric, or hydrochloric, as may be most appropriate) instead of standard alkali as the titrating fluid. When the alkali contains carbonates, as is generally the case, the carbonic acid is liberated, and colors the litmus pale red. The following modification of the process then becomes necessary: Add standard acid from the burette until the pale-red color makes its appearance. Then cover the beaker with a watch-glass, and heat to boiling over the lamp. The carbonic acid is in this way decomposed, carbon dioxide is driven off, and the litmus again becomes blue. Now add acid until the red color reappears, heat again to boiling, and repeat this until the red color is changed to blue by boiling the solution. When this point is reached, the titration is completed. A more rapid and equally exact method is to add an excess of acid in the first place, then boil the solution until all carbonic acid is driven off, and then run in standard alkali from another burette until the blue color makes its appearance. The end of the reaction by this method is very sharply shown.

Where carbonates are present, cochineal is a better indicator than litmus, since it is only slightly affected by the liberated carbonic acid. Normal acid is added to the alkaline solution, containing a few drops of cochineal solution, until the color changes to yellow. After boiling off the carbonic acid, but two or three drops more acid are required to restore the yellow color and complete the reaction.

Titrations with litmus as indicator may be conducted at night by the light of the monochromatic flame produced by heating a platinum wire or piece of asbestos dipped in a solution of sodium chloride in the colorless flame of a Bunsen lamp. The change of color in the litmus is easily seen and sharply defined. The red solution, under these circumstances, appears entirely colorless, while the blue solution is black and opaque. Strongly colored acid or alkaline fluids may be titrated with litmus by the monochromatic flame with greater exactness than by daylight.*

Sodium carbonate and oxalic acid are used as the basis of analysis by saturation, since it is easy, by using pure reagents and careful weighing, to obtain solutions which are exactly normal. The other solutions are then compared with these by the method given above. Other methods of checking the accuracy of the standard solutions will suggest themselves, and may be applied when great accuracy is desirable.

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* L. D. Henry, Comptes Rendus, 76, 222.

KIEFFER'S METHOD.*

For the Estimation of the Free Acid in Presence of Metallic Salts.

In the presence of many salts of the heavy metals, copper, iron, zinc, etc., it is impossible to estimate the amount of free acid present by the ordinary method, because the metallic salt itself colors litmus red, and the blue color is not produced until the metal is completely thrown down. For determining free acid in presence of these salts, Kieffer uses an ammoniacal solution of copper sulphate, prepared by dissolving a quantity of copper sulphate in water, and adding ammonia until the precipitate at first formed is nearly, but not completely, redissolved. The solution is then filtered and diluted to the proper strength. Its strength is determined as follows: A measured volume of normal acid (not oxalic) is measured out and the ammoniacal copper solution run in until the acid is saturated, when the fluid becomes turbid by the separation of a greenish precipitate, supposed to be a basic copper sulphate, which serves as the indicator.

This method does not answer in presence of salts of aluminum, or of ferric, chromic, or manganic salts. If copper nitrate be used in making the solution, instead of copper sulphate, salts of barium, strontium, and lead may be present. The method is sufficiently accurate for technical purposes, but is not exact enough for work requiring great accuracy.

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* Liebig's Annalen, 93, 386.

Large quantities of ammoniacal salts are objectionable, as they dissolve the precipitate of copper subsulphate formed at the end of the process. The solution alters in strength slowly, and must be restandardized before each series of determinations.

PETTENKOFER'S METHOD.*

Pettenkofer uses a method for the estimation of carbonic acid which is equally applicable to other acids, and the results obtained are remarkably sharp. Solution of barium hydrate is the saturating agent used, and for estimating an excess of this $\frac{n}{10}$ oxalic or hydrochloric acid. The indicator is turmeric paper, which shows the smallest excess of barium hydrate.

Solution of barium hydrate is prepared from the crystallized hydrate, or by heating barium nitrate to redness, and dissolving the resulting oxide in water. The solution should be nearly saturated, but not so strong as to deposit crystals when exposed to low temperatures. It must be free from potassium or sodium hydrate, and should be kept in the bottle (Fig. 24), to preserve it from the carbonic acid contained in the air, which would precipitate the barium as carbonate.

The solution is measured by means of a pipette (Fig. 26) provided with a tube containing soda, lime, or fragments of the ignited mixture of lime and sodium sulphate. This prevents the carbonic acid of the breath from coming in contact with the solution.

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* Jour. für Prak. Chemie, 82, 33; 82, 40; 85, 165; 85, 179; see also Gottlieb, *Ib.* 107, 488.

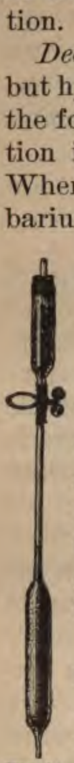

FIG. 26.

Decinormal Acid.—This is preferably oxalic acid, but hydrochloric also answers and keeps better than the former, which is especially liable to decomposition if a trace of ferric oxide be present (Mohr). When oxalic acid is employed, a precipitate of barium oxalate is produced on adding it to the solution of barium hydrate, but this does not interfere in the least with the working of the process.

Turmeric Paper.—Pieces of turmeric are digested in alcohol and the solution filtered. Pieces of white filtering paper are soaked in the alcoholic extract, dried in a dark place, and kept in a stoppered bottle or between the leaves of a book. Acids have no effect upon this paper, but solutions containing hydrates of the alkaline or alkaline-earth metals color it brownish red.

The Analysis.—The strength of the barium hydrate solution is first found by comparison with the decinormal acid. For this purpose, 10 c. c. are taken out by means of the pipette (Fig. 26), and $\frac{n}{10}$ acid slowly run in from the burette. From time to time, a small drop is taken out with the point of a glass rod, and the turmeric paper touched with it. As long as the slightest excess of barium hydrate is present, a reddish brown spot is produced, but when the last trace of barium hydrate is saturated, the color remains unchanged. The end of the reaction is very sharply shown. When the amount of acid in a solution is to be estimated, a volume of barium hydrate in excess is added from the pipette, and the excess measured by titration with $\frac{n}{10}$ acid. The process is especially useful for the determination of carbonic acid, and for testing dark-colored vinegars, etc., where, on account of the color, litmus cannot be used.

ESTIMATION OF THE ACID IN NEUTRAL SALTS.[*]

The metallic base of the salt in which the acid is to be estimated, must be capable of being completely precipitated from solution by means of alkaline hydrate or carbonate.

The solution is treated with an excess of normal sodium hydrate or carbonate, and boiled, if necessary, to precipitate the metallic oxide, then filtered and washed, and the excess of alkali in the filtrate determined by means of litmus and normal acid.

A more rapid but slightly less accurate method is to precipitate as above, pour the solution and precipitate into the same measuring flask, allow the precipitate to settle completely, and take out a portion of the supernatant liquid for titration with a pipette. The acid in the following compounds may be thus estimated:

Salts of barium, calcium, aluminum, magnesium, zinc, iron, and manganese, by boiling with normal sodium carbonate.

Salts of bismuth, nickel, cobalt, and lead, in the same way, but they must be boiled for at least half an hour.

Salts of magnesium, copper, silver, iron, mercury, and chromium, by boiling with sodium hydrate. Wolcott Gibbs * has announced another method for this estimation, which depends upon the precipitation of the metal by means of sulphydric acid in the boiling solution, filtering from the precipitated sulphide, and determining the acid in the filtrate by normal alkali. The estimation of course can only be made in those salts whose base is completely precipitated from boiling solution by sulphydric acid.

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[*] Liebig's Annalen, 117, 230.

In the case of nitrates or chlorides, where the free acid tends to re-dissolve the precipitated sulphide or to act on the sulphydric acid, Gibbs adds a tolerable quantity of sodium, or potassium tartrate, or Rochelle salt, which obviates all difficulty.

The chief objection to this method is the employment of the offensive sulphydric acid, which should be avoided whenever it is possible.

Bohlig † has proposed a method for the estimation of alkaline sulphates, based upon the decomposition of barium carbonate in presence of an alkaline sulphate and free carbonic acid, into barium sulphate—an alkaline carbonate being at the same time formed. By the reverse process, barium compounds are precipitated as carbonates, and then decomposed by solution of potassium sulphate in presence of free carbonic acid.

Chlorides, bromides, and iodides of the alkaline metals are determined by shaking them with an excess of silver carbonate, which removes the chlorine,

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* Chem. News, xvii. 151; Silliman's Journal (II.), 44, 207; Fres. Zeitschrift, 7, 94.

† Fres. Zeitschrift, 1870, 310.

bromine, or iodine completely, and leaves the alkaline metal in solution as carbonate. For particulars the student is referred to the original article, Arch. Pharm. 3, cxlv. 113, or to a summary of the process, which will be found in the Journal of the Chemical Society, 1871, p. 436; see also Arch. Pharm. [3] iii. 122; Jour. Chem. Soc., 1874, 815.

Jean* proposes a similar method for the determination of sulphuric acid in alkaline sulphates. The sulphuric acid is precipitated by an excess of baryta water, the excess of baryta precipitated by Seltzer water, the precipitate separated by decantation, boiled, and filtered with the first precipitate. The alkali is then determined in the filtrate, and represents that combined with the sulphuric acid.

OXIDATION OR REDUCTION.

Solutions Used—Potassium Permanganate.

Decinormal Solution = 3·162 gms. $KMnO_4$ per litre.

The salt of commerce may be used for making the solution. It is best kept in a dark place or in covered bottles. Preserved in this way, it alters very little in strength. After determining the strength and diluting until exactly tenth normal, it may be used for several months without a fresh determination being made.

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* Comptes Rendus, lxxxiii. 973; Jour. Chem. Soc., Vol. 1, 1877, 738.

Potassium permanganate in solution, in contact with a substance capable of being oxidized and an acid—sulphuric, for example—is decomposed as represented in the following equation:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2\,(MnSO_4) + 5.O.$$

The manganese sulphate formed is colorless in dilute solution, and consequently the fluid to which the potassium permanganate is added remains colorless until the body present is completely oxidized, when the next drop of permanganate will color the fluid and show the reaction to be completed. This reaction is extremely sharp, and gives excellent results.

Determination of the strength—

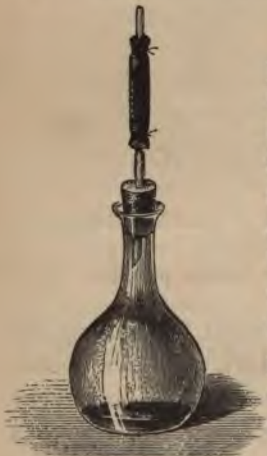

Fig. 27.

1. By metallic iron.

The iron used for this purpose must be in the form of the finest iron wire. It must leave no residue whatever when dissolved in acid, and the solution of iron must be entirely free from small black particles. These consist of carbon contained in the iron, and are oxidized by the permanganate if present, causing a considerable error.* A piece of iron wire weighing about ·2 gms. is placed in a flask provided with a cork and valve like Fig. 27. The small thick walled rubber tube has a short slit made lengthwise through one of the walls and the upper end closed by a piece of glass rod. This valve opens by pressure from within, but closes by pressure from without. Dilute *sulphuric* acid is added, and the flask heated over the lamp until the iron wire is dissolved. Allow it to cool perfectly, add fresh, cold distilled water until the flask is half filled, and run in permanganate from the burette, with constant shaking of the flask until the liquid has a faint pink color. It is advisable to add only just sufficient excess of permanganate to the liquid to make the color visible. The action of the permanganate upon the iron may be thus represented:

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* Chemical News, xxx. 142.

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Instead of the flask Fig. 27, one arranged as in Fig. 28 may be used, and is for many reasons to be preferred. While the iron is dissolving in the flask, a current of hydrogen (not illuminating gas) is passed through it, entering by *a* and passing out by *b*. This arrangement affords greater security against oxidation, and has other advantages, the chief of which is that there is no danger of breaking the flask containing the iron solution. This not unfrequently happens where the flask with valve is used: the steam generated by heating forcing out the air, and this subsequently condensing produces a vacuum.

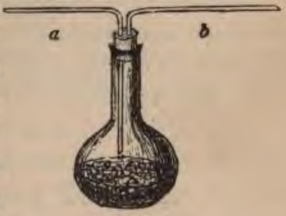

FIG. 28.

If the sides of the flask are thin, the inward pressure crushes them, causing total loss of the analysis.

2. With oxalic acid.*

About 3 gms. crystallized pure oxalic acid are dissolved in distilled water, dilute sulphuric acid added, the solution heated to 60° or 80°, and permanganate run in from the burette. The color of the permanganate disappears more slowly than with the solution of iron, and it must be added slowly and the solution stirred continually. When the titration is performed carefully and the oxalic acid pure, the method is an excellent one for standardizing.

The action of permanganate upon oxalic acid is as follows:

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 8H_2O + 10CO_2 + K_2SO_4 + 2MnSO_4.$$

Ammonium oxalate $(NH_4)_2C_2O_4 + H_2O$ may also be used to estimate the strength of the permanganate. It is more easily obtained pure than oxalic acid.

3. With ferrous ammonium sulphate.

About 1 gm. ferrous ammonium sulphate, prepared as described page 51, is dissolved in water, dilute H_2SO_4 and water added, and permanganate run in with constant stirring until the solution remains permanently faintly colored.

These three methods are almost equally good, and either or all may be used. When preparing permanganate solution, it is well to make it in large quantities, and to determine its strength by two of the methods here given. The solution, if preserved from the light, may be used without fear of having changed in strength for at least three months, when it may be tested again.

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* For methods of purifying oxalic acid, in addition to the one given under Normal Oxalic Acid, see Fres. Zeitschrift, 13, 49.

The oxalic acid or ammonium oxalate, and ferrous ammonium sulphate, if carefully prepared, may be considered pure, and the strength calculated on that basis. The iron wire, however, always contains impurities, which in the best very thin iron wire are nearly constant in amount. The wire may be assumed without sensible error to contain 99·7 % pure iron, and the following proportion gives in any case by a slight calculation the amount of pure iron in a given piece of wire taken:

$$100 : 99\cdot7 :: \text{weight of wire taken} : x.$$

One c.c. decinormal solution of permanganate should oxidize

·0056 gms. Fe.
·0063 " $H_2C_2O_4$, or ·0071 gms. $(NH_4)_2C_2O_4 + H_2O$.
·0392 " ferrous ammonium sulphate.

POTASSIUM BICHROMATE.

Decinormal Solution = 4·9205 gms. $K_2Cr_2O_7$ per litre.

This salt may be obtained in large crystals, which are nearly pure. They may be purified from potassium sulphate, which they sometimes contain, by recrystallization. The salt contains no water of crystallization, and may be fused without decomposition. About 5 gms. of the finely-powdered salt is placed in a platinum crucible heated nearly to fusion, allowed to cool under the desiccator, and exactly 4·9205 gms. weighed out, dissolved in water, and diluted to a litre.

The use of this salt as an oxidizing agent depends upon the following reaction in presence of an oxidizable substance and free acid.

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

The strength of the solution is best determined by means of metallic iron in the form of wire, which in this case may be dissolved in either sulphuric or hydrochloric acid. Unfortunately with bichromate, the end of a reaction cannot be determined by means of the permanent yellow coloration of the solution, since the chromium sulphate formed is of a green color. Recourse must, therefore, be had to an indicator, and potassium ferricyanide is used where we are titrating against ferrous salts, as is usually the case. When a drop of solution containing a ferrous salt is brought in contact with a drop of potassium ferricyanide solution, a deep blue color is obtained. As soon as the ferrous salt is completely oxidized, by addition of bichromate, to the ferric state, a drop brought in contact with a drop of ferricyanide no longer produces the blue color, but only a faint brownish tint.

The bichromate solution is standardized as follows: About 2 gms. iron wire is dissolved in sulphuric or hydrochloric acid in one of the flasks (Figs 27 or 28), water added, and bichromate run in gradually from the burette. From time to time a drop of the solution, which gradually assumes a greenish tint, is taken out by means of a glass rod, dropped on a porcelain plate, and a drop of potassium ferricyanide brought in contact with it. As the iron is oxidized, the drops taken out are less strongly colored by addition of the ferricyanide, until at last only a faint brownish color is produced. The reaction is then finished. With very little practice, it becomes easy to hit this point exactly, and the results are very sharp and exact. The amount of fluid taken out is so small that it exercises no appreciable influence on the results. One c. c. of bichromate solution should be equal to ·0056 gms. iron, or ·0392 gms. ferrous ammonium sulphate.

Potassium bichromate is generally used in connection with a ferrous salt; either iron wire dissolved in hydrochloric or sulphuric acid, or a solution of ferrous ammonium sulphate. An excess of the ferrous salt is added to a substance capable of oxidizing the iron to the ferric state, and the excess of ferrous salt determined by bichromate. Its frequent use is due to the fact that it may be used in presence of hydrochloric acid, which is not the case with permanganate.

FERROUS AMMONIUM SULPHATE.

Decinormal Solution = 39·2 gms. $Fe(NH_4)_2(SO_4)_2 + 6H_2O$ per litre.

One atom ferrous sulphate ($FeSO_4 + 7H_2O = 278$ parts) and 1 atom ammonium sulphate ($(NH_4)_2SO_4 = 132$ parts) are dissolved in the smallest possible quantities of hot water, filtered if necessary, and the solutions mixed and allowed to cool with constant stirring. A fine greenish-white crystalline precipitate results, which is ferrous ammonium sulphate $Fe(NH_4)_2(SO_4)_2 + 6H_2O$. This is placed on a filter, the mother liquor sucked off by means of the Bunsen filter pump, and then pressed between filter paper, and allowed to dry in the air. After the salt is perfectly dry, 39·2 gms. are weighed out, dissolved in water which has been boiled and allowed to cool in a closed flask, 10 c.c. pure concentrated sulphuric acid added, and the solution diluted to a litre with boiled distilled water. The remainder of the salt may be preserved in a wide-mouthed stoppered bottle, and keeps indefinitely. If the solution is allowed to stand in contact with the air, it absorbs oxygen slowly, and it must therefore be kept in the bottle, Fig. 29. A layer of petroleum, half an inch thick, is poured upon the surface of the liquid, and prevents the action of the oxygen of the air upon it. Preserved in this way, the solution keeps without alteration. The strength of the solution may be determined by taking about ·2 gms. pure potassium bichromate, heating nearly to fusion, and then allowing to cool under the desiccator. The exact weight is now found; the salt dissolved in water, hydrochloric or sulphuric acid added, and

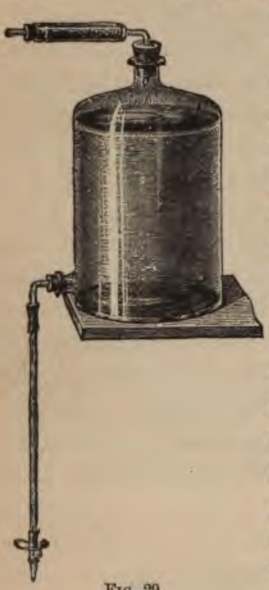

FIG. 29.

the ferrous solution run in from a burette until a drop taken out strikes a faint blue color with potassium ferricyanide. One c. c. of the ferrous ammonium sulphate solution should be equal to ·00492 gms. $K_2Cr_2O_7$.

Iodine Solution.

Decinormal Solution = 12·685 gms. I per litre.

The iodine for making this solution should be purified by mixing with a small portion of potassium iodide, and subliming. The sublimation may be performed between two watch-glasses. The iodine rises in vapor, and condenses perfectly pure upon the upper glass. It is dried in the desiccator and 12·685 gms. are then weighed into the litre flask. Since iodine is only slightly soluble in water, we must add about 18 gms. pure potassium iodide in order to dissolve it. The solution is made up to a litre, carefully shaken to insure uniformity, and preserved in small bottles with glass stoppers carefully ground. The potassium iodide used must be free from iodate. To make sure of this, dissolve a small quantity in water, and then add some hydrochloric acid and a little starch solution. A blue color indicates the presence of iodate. This may be removed, if present, by heating to redness, when oxygen is evolved, and the iodate reduced to iodide.

A centinormal solution is frequently used, and may be made by diluting 100 c. c. decinormal solution to a litre.

Iodine acts as an oxidizing agent in many cases by acting upon water to form hydriodic acid, and setting free oxygen which combines with the oxidizable substance. For example:

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI.$$

Sometimes it acts as an oxidizing agent only by extracting hydrogen, as for example:

$$H_2S + 2I = 2HI + S.$$

In either case it is easy to tell when the reaction is complete by adding a little starch solution to the fluid, which is turned blue as soon as the change is effected, and a slight excess of free iodine present.

Standardizing the Solution.—The solution may be standardized in two ways:

1. By sodium thiosulphate.

About ·8 gms. of the pure crystallized salt is dissolved in water, and a few drops of the starch solution added. The iodine solution is then run in from the burette. Each drop forms a blue spot as it touches the fluid, but this disappears, at first rapidly; then, as the end of the reaction approaches, more and more slowly; and finally the whole fluid is of a faint blue color. Only a very small excess of iodine is necessary to color the liquid strongly. The reaction between the iodine and thiosulphate is as follows:

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$

Sodium tetrathionate and iodide are the products.

One c. c. of the iodine solution should oxidize ·024808 gms. sodium thiosulphate.

2. By arsenious acid.

About ·2 gms. pure pulverized arsenic trioxide is dissolved with the aid of heat in a solution of ammonium carbonate, and a few drops of solution of starch added. The iodine is run in from a burette until the blue tint is produced. The reaction is the same as before given. One c. c. iodine should = $\cdot 00495$ As_2O_3.

Starch Solution.—A small quantity of starch is rubbed in a mortar with a little cold water until an emulsion is produced; it is then poured into about 100 times its volume of boiling water. The solution is allowed to stand until the fluid becomes clear and undissolved particles subside. The fluid is then poured off and completely saturated with pure common salt, filtered, and preserved in small stoppered bottles filled completely.* Such a solution keeps well and is always ready for use. Starch solution is used to indicate the presence of free iodine in a solution: the merest trace imparting a deep blue color to the liquid. The blue color disappears at a temperature of 80°, but again appears on cooling.

SODIUM THIOSULPHATE.

Decinormal Solution = 24·8086 gms. $Na_2S_2O_3 + 5H_2O$ per litre.

This salt may be obtained in commerce sufficiently pure for use. It may be purified by recrystallization, if thought desirable. The crystals are dried between filtering paper, 24·8086 gms. weighed out, dissolved in water, and diluted to a litre. The solution does not keep well, and gradually decomposes with evolution of H_2S and deposition of S.

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* According to Mohr, starch solution may be preserved indefinitely by adding a little salicylic acid to the solution. See Fres. Zeitschrift, 14, 79.

According to Mohr, an addition of ammonium carbonate (the ordinary commercial carbonate of ammonia), to the extent of 2 gms. per litre, entirely prevents this decomposition, and does not interfere with the application of the solution. It is convenient to have, also, a centinormal solution, which may be made by diluting 100 c.c. decinormal solution to a litre.

When one of the higher oxides, manganese dioxide, for example, is treated with potassium iodide and hydrochloric acid, the following reaction takes place:

$$MnO_2 + 4HCl + 2\,KI = MnCl_2 + 2H_2O + 2KCl + 2I.$$

The iodine which is set free dissolves in the excess of potassium iodide. The free iodine can now be estimated by adding, first, starch solution, which produces the deep blue color, and then decinormal sodium thiosulphate, until the blue color disappears: the reaction being as follows:

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

When, as is often the case, heat must be applied to assist the action of the acid and potassium iodide upon the oxide to be determined, the three substances are placed in the bottle shown in Fig. 30. The stopper of this bottle must be ground very accurately, and this may be tested by closing it and immersing in warm water, when, if the stopper is not tight, small bubbles of air escape around it. The bottles which are made for use in the silver assay by the wet method answer admirably for this purpose. The bottle with its contents is placed in its frame, and the screws turned until the stopper is securely held in place. The bottle is then immersed in water, which is brought to a boil, and, after the reaction is completed, removed, and the contents titrated with thiosulphate.

In many cases it is better to distil the oxide with hydrochloric acid, which sets chlorine free, in an amount proportional to the oxide present. The chlorine is conducted into a solution of potassium iodide, which absorbs it, liberating iodine which dissolves in the excess of potassium iodide, and is estimated by thiosulphate.

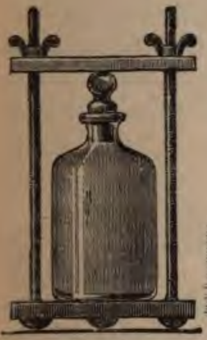

FIG. 30.

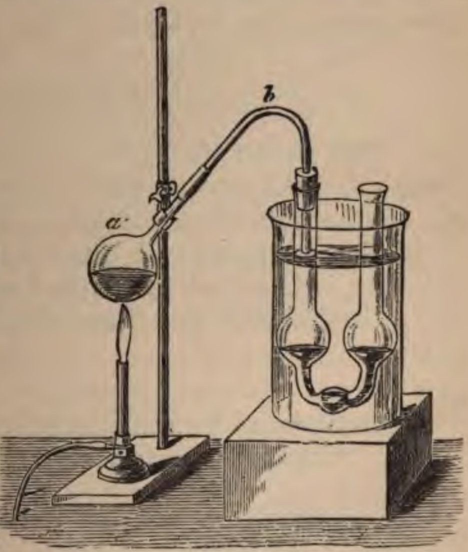

FIG. 31.

The best form of apparatus for this distillation is shown in Fig. 31; *a* contains the substance to be analyzed and hydrochloric acid. It is connected with the U tube, which contains the potassium iodide, by means of a piece of rubber tubing, which has been boiled in potassium hydrate to free it from sulphur. The bulbs on the U tube are intended to prevent the contents from being ejected or sucked back into the flask. After the oxide is completely decomposed and chlorine ceases to come off, the apparatus is disconnected, the contents of the U tube washed into a flask or beaker, a little fresh potassium iodide introduced, and the apparatus again put together, and the distillation continued for a few minutes. This second distillation is carried on only long enough to make sure that the chlorine is all given off. If the potassium iodide used in this second distillation becomes at all colored from separation of iodine, it is added to the first portion, and the whole titrated with starch and decinormal thiosulphate.

STANDARDIZING THE STRENGTH OF THE DECINORMAL SODIUM THIOSULPHATE.

1. *With Iodine.*—Pure iodine, prepared by sublimation in the manner described on page 53, is dried under the desiccator, and about ·4 gms. weighed out and dissolved in a little potassium iodide and water. A few drops of starch solution are added, and then sodium thiosulphate run in until the blue color is discharged. ·1 c. c. thiosulphate should = ·012685 I.

2. *With Potassium Bichromate.*—About ·2 gms. pure bichromate previously heated nearly to fusion,

to free it from hygroscopic moisture, is weighed into the bottle (Fig. 30), dissolved in water, hydrochloric acid, and an excess of potassium iodide added, and the stopper inserted and fastened down. The bottle is then placed in warm water until heated through, taken out and allowed to cool, and the solution poured into a beaker, rinsed out, starch added, and titrated with the thiosulphate solution.

1 c.c. thiosulphate should = ·00492 bichromate.

SODIUM ARSENITE.

Decinormal Solution = 4·95 gms. As_2O_3 per litre.

Dissolve 4·95 gms. of the purest sublimed arsenious oxide which does not contain sulphide, in about 250 c.c. of distilled water in a flask, with about 25 gms. of the purest sodium carbonate, free from sulphide, sulphite or thiosulphate. The arsenious oxide must be in fine powder, and takes some time to dissolve. It is best to heat and shake from time to time, to assist the solution. When all is dissolved, allow to cool, wash into the flask, and dilute to a litre. The arsenious oxide may be tested for sulphur by placing a little in a test tube and subliming. If the upper part of the sublimate have a yellow color, sulphur is present, and the arsenious oxide unfit for the purpose. If the arsenic trioxide and the sodium carbonate be pure, the solution keeps without any alteration in strength.

The use of sodium arsenite depends upon the following reaction of arsenious acid in alkaline solution:

$$As_2O_3 + O_2 = As_2O_5.$$

Solution of sodium arsenite is used chiefly in the estimation of the active chlorine in bleaching powder where thiosulphate cannot be used.

The strength is best estimated by taking 10 c.c. of the solution, adding a few drops of starch and then $\frac{n}{10}$ iodine solution, until the blue color appears. 1 c.c. As_2O_3 solution should = 1 c.c. $\frac{n}{10}$ iodine.

STANNOUS CHLORIDE.

Decinormal Solution = 5·9 gms. Sn or 9·45 gms. $SnCl_2$ per litre.

The best method of preparing this solution is to dissolve about 6 gms. pure granulated tin in strong pure hydrochloric acid. If one or two scraps of platinum foil be added to the hydrochloric acid, galvanic action occurs: the tin being rapidly dissolved without application of heat. If no platinum foil is added, the tin does not dissolve in the cold, and the solution must be boiled until the tin has disappeared.

The solution should be kept in the bottle Fig. 29. In order to preserve it against the oxidizing action of the air, a thin layer of refined petroleum is poured upon the surface of the liquid.

Its strength is best estimated against metallic iron.

Dissolve about ·2 gms. iron wire in hydrochloric acid in a beaker covered with a watch glass, add a few crystals of potassium chlorate to oxidize the iron, and after washing off the watch glass, allow the solution to evaporate almost to dryness. Add a little water, heat over the lamp, and add the stannous chloride from the burette until the red color of the iron salt has disappeared, and the solution is perfectly colorless. It is difficult here to avoid adding a slight excess of stannous chloride, and to ascertain what this excess amounts to, we proceed as follows:

After stannous chloride has been added until the solution loses color, the beaker is immersed in cold water, and the solution rapidly cooled: starch solution is then added and iodine solution run in from a burette until the color makes its appearance. We must now determine how much stannous chloride the iodine added is equal to. To do this run 10 c.c. of the stannous chloride into a beaker, add starch, and titrate with iodine until the blue color appears. If the solutions are both decinormal, 10 c. c. of iodine will be required.

Suppose, now, we have added 36 c. c. of stannous chloride to the iron solution, then starch, and ·5 c. c. iodine before the blue color appears. By experiment we find 10 c. c. stannous chloride = 10·2 c. c. I; then 1 c. c. I will = ·98 c. c. $SnCl_2$ and ·5 c. c. I = ·49 c. c. $SnCl_2$; 36 c. c. — ·49 c. c. = 35·51 c. c. $SnCl_2$ are therefore = to the amount of iron wire taken. This weighed ·2 gms., and without sensible error may be supposed to contain 99·7% or ·1994 gms. pure iron. Hence

35·51 c. c. = ·1994 gms.

and 1 c. c. = ·00561 gms. Fe.

1 c. c. $\frac{n}{10}$ solution should = ·0056 Fe, and the solution is hence a trifle too strong.

PRECIPITATION.

SOLUTIONS USED.

VERY few of the solutions used under this heading are of wide application, and the methods of preparing and standardizing them will be given under the substance for the estimation of which they are used.

1. The reagent is added until a precipitate ceases to form.
2. The reagent is added until a precipitate is produced.
3. The reagent is added until a precipitate already formed, redissolves.

In the second and third cases it is easy to hit the precise point when the reaction is terminated, but in the first case the precipitate formed, which remains suspended in the liquid, prevents the subsequent precipitation from being seen. In this case, it becomes necessary either to free the fluid, or a part of it, from the suspended precipitate, when, by adding a small portion of the reagent, we can see whether precipitation is complete, or, we must bring an indicator, which will show an excess of the precipitant in contact with a drop of the solution.

The method adopted depends upon the circumstances of the case. Where chlorine is estimated by means of silver nitrate, or conversely silver by sodium chloride, the precipitated silver chloride which is formed subsides rapidly if the solution containing it be violently agitated, and by adding a drop of the standard solution to the clear supernatant fluid, it is easy to see whether the precipitation is completed. There are very few precipitates, however, which possess this property in a marked degree; and in other cases it becomes necessary, by some special contrivance, to filter a small portion of the liquid, and add a drop of the reagent to the clear fluid thus obtained. Dr. Beales's filtering tube has the form shown in Fig. 32. It consists of a piece of tubing the width of an ordinary test-tube, and having a filter fastened over the lower end. The filter is made by laying a piece of linen over the opening, then a piece of filtering paper, and lastly, a piece of linen over this, and tying the three tightly by a waxed thread. On placing this filtering tube in a turbid liquid, the fluid rises through the filter perfectly clear, and a portion may then be poured off from the side tube and tested. This tube is very objectionable in practice, since it is liable to clog quickly, cannot be washed out with ease, and is apt to break. For these reasons the tube shown in Fig. 33 is much to be preferred. It is made of a piece of glass tubing about 6 millimetres in diameter. This is drawn to a point, and a small plug of asbestos inserted. The tube is then drawn out over this, and the part of the tube containing the asbestos then heated strongly in a glass-blower's lamp so as to soften the glass and cause the asbestos to adhere to it. To use the filter-

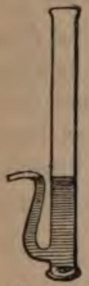

FIG. 32.

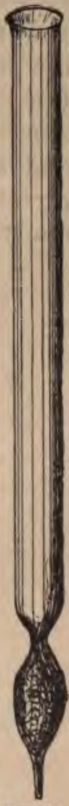

FIG. 33.

ing pipette, place the point in the turbid fluid and apply suction with the mouth. This causes the fluid to rise into the tube, and by passing through the asbestos all solid particles are removed. Upon blowing into the tube, the liquid is now forced out, and, after the first few drops, the fluid falling from the point is perfectly clear, and suitable for testing. For this purpose it is received in a small test tube about 8 mm. in diameter, and 4 centimetres long, and a drop of the reagent added. The filtering pipette is easy to make and to clean, and is always ready for use.

PART II.

POTASSIUM.

POTASSIUM HYDRATE.

THE amount of potassium oxide in a solution of the pure substance may be found by taking the specific gravity. Comparison of this with the figures in the following table gives the percentage in K_2O, and from this the percentage of KOH may be obtained by the following proportion, 47·137 : 56·137 : : % K_2O : % KOH.

TABLE.*

Showing the amount of K_2O in Potassa Lye of different specific gravities. Temp. 17·5°.

K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.
45·0	1·576	39·5	1·492	34·0	1·414	28·5	1·339
44·5	1·568	39·0	1·484	33·5	1·407	28·0	1·332
44·0	1·560	38·5	1·477	33·0	1·400	27·5	1·326
43·5	1·553	38·0	1·470	32·5	1·393	27·0	1·320
43·0	1·545	37·5	1·463	32·0	1·386	26·5	1·313
42·5	1·537	37·0	1·456	31·5	1·379	26·0	1·307
42·0	1·530	36·5	1·449	31·0	1·372	25·5	1·301
41·5	1·522	36·0	1·442	30·5	1·365	25·0	1·294
41·0	1·514	35·5	1·435	30·0	1·358	24·5	1·288
40·5	1·507	35·0	1·428	29·5	1·352	24·0	1·282
40·0	1·500	34·5	1·421	29·0	1·345	23·5	1·275

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* **Hoffman, Schaedler, Tabellen für Chemiker, p. 119.**

TABLE—(*Continued*).

K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.	K_2O per cent.	Specific Gravity.
23·0	1·269	17·5	1·201	12·0	1·135	6·5	1·070
22·5	1·263	17·0	1·195	11·5	1·129	6·0	1·065
22·0	1·257	16·5	1·189	11·0	1·123	5·5	1·059
21·5	1·250	16·0	1·183	10·5	1·117	5·0	1·054
21·0	1·244	15·5	1·177	10·0	1·111	4·5	1·048
20·5	1·238	15·0	1·171	9·5	1·105	4·0	1·042
20·0	1·231	14·5	1·165	9·0	1·099	3·5	1·037
19·5	1·225	14·0	1·159	8·5	1·094	3·0	1·031
19·0	1·219	13·5	1·153	8·0	1·088	2·5	1·026
18·5	1·213	13·0	1·147	7·5	1·082	2·0	1·021
18·0	1·207	12·5	1·141	7·0	1·076	1·5	1·015

Method of Saturation.

Weigh out 10 gms. of the hydrate, dissolve in water in the half litre flask and fill the flask to the mark, shake thoroughly and allow any sediment to subside. Take out 50 c. c. with a pipette, add litmus and run in normal acid until the blue color changes to red.*

When Carbonic Acid is present.

Dissolve in water as above, heat to boiling, add sufficient barium chloride to precipitate all the carbonic acid, allow to cool, dilute to 500 c. c., allow the barium carbonate to subside, take out 50 c. c. and titrate as above. When the sample contains a large amount of carbonic acid, the volume of the precipitate being neglected causes a considerable error.

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* For the estimation of alkalies Stolba (Fres. Zeit. 11, 199) uses a decinormal solution of sodium silicofluoride containing 4·7 gms. per litre (compare p. 73).

In such cases it is better to take a smaller portion of the hydrate, say 1 gm., for analysis, dissolve in water in a flask, heat to boiling, add the barium chloride in excess, allow the precipitate to settle, decant the fluid on a filter, fill the flask with water and wash the precipitate by decantation twice or three times: then bring the precipitate on the filter and wash rapidly until the washings no longer turn red litmus paper blue. The filtrate is then titrated with normal acid in the usual way. The filtration must be performed rapidly or carbonic acid will be absorbed from the air.

c. c. normal acid × ·039137 = K
" " " × ·047137 = K_2O
" " " × ·056137 = KOH

Calculation.

Suppose 9·9432 gms. potassium hydrate were taken for analysis, dissolved in 500 c. c. water, and 50 c. c. taken out for titration, ·15·2 c. c. normal acid were required. The 50 c. c. taken for titration contained ·99432 gms. potassium hydrate or $\frac{1}{10}$ the amount weighed out. For saturation this took 15·2 c. c. normal acid, which × by ·056137 = ·8532824 KOH or 90·48 %.

POTASSIUM CARBONATE.

The strength of solutions of the pure salt may be found by taking the specific gravity and comparing with the following table:

TABLE.

Hoffman, Schaedler, Tabellen für Chemiker, p. 119.

Showing the amount of Dry Potassium Carbonate in solutions at 15°, according to Tünnermann.

Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity	Per cent.
1·4812	40·504	1·3585	30·349	1·2282	19·580	1·0940	8·811
1·4750	40·139	1·3480	29·360	1·2150	18·601	1·0829	7·832
1·4626	39·160	1·3378	28·391	1·2020	17·622	1·0719	6·853
1·4504	38·181	1·3277	27·412	1·1892	16·643	1·0611	5·874
1·4384	37·202	1·3177	26·432	1·1766	15·664	1·0505	4·895
1·4265	36·223	1·3078	25·454	1·1643	14·685	1·0401	3·916
1·4147	35·244	1·2980	24·475	1·1520	13·706	1·0299	2·934
1·4030	34·265	1·2836	23·496	1·1400	12·727	1·0108	1·958
1·3915	33·286	1·2694	22·517	1·1282	11·748	1·0098	0·978
1·3803	32·307	1·2564	21·538	1·1166	10·768	1·0048	0·489
1·3662	31·328	1·2417	20·539	1·1052	9·790		

By Saturation.

Dissolve about 10 gms. of the sample in water, pour into the half litre flask, and allow to settle; fill to the mark with water, take out 50 c.c. of the clear fluid with the pipette, add litmus, and run in normal acid until the color becomes reddish; the fluid is then boiled for a few seconds, and if the litmus becomes blue again, acid added until the red color appears. This process is repeated until boiling ceases to restore the blue color. Cochineal is in this case preferable to litmus as an indicator. Or the following method may be used:

Add at once a quantity of normal acid more than sufficient to saturate the potassium present; boil the solution to drive off carbonic acid, and then run in normal alkali until the blue color makes its appearance. The number of c. c. of acid used − the number of c. c. of normal alkali = the number of c. c. of acid necessary for saturation.

When it is desired to ascertain the total amount of potassium in a mixture of hydrate and carbonate, the analysis is to be performed exactly as though carbonate only were present.

c. c. normal acid × ·039137 = K
" " " × ·056137 = KOH
" " " × ·069137 = K_2CO_3

POTASSIUM CHLORIDE.

The weighed substance containing no other chloride is brought into solution, and the chlorine estimated by $\frac{n}{10}$ silver nitrate. (See Chlorine.)

c. c. $\frac{n}{10}$ silver solution × ·0039137 = K
" " " " × ·0056137 = KOH
" " " " × ·0074594 = KCl
" " " " × ·0069137 = K_2CO_3

All compounds of potassium may be converted into the chloride, and estimated as above, either

1. By evaporation to hard dryness with hydrochloric acid, or

2. By precipitation as double chloride of platinum and potassium $(KCl)_2PtCl_4$, and then converted into the chloride by ignition with twice the weight of sodium oxalate.

The platinum is reduced to the metallic state, its chlorine combining with the sodium of the sodium oxalate. The excess of oxalate is converted into carbonate by the ignition. The mass is dissolved in water, filtered, neutralized with acetic acid, and the chlorine determined with $\frac{n}{10}$ silver solution.* The result here obtained must be divided by 3, since $(KCl)_2PtCl_4$, by ignition with the oxalate, gives $2KCl + 4NaCl + Pt$. Small quantities of potassium sulphate may be converted into chloride by heating with ammonium chloride until the excess is driven off. The ignition must be repeated several times before the decomposition is complete. Care must be taken not to raise the temperature above low redness, otherwise a portion of the potassium chloride volatilizes.†

Specific gravity of solutions of Potassium Chloride at 15°. *Water at* 15° = 1.‡

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00650	13	1·08654
2	1·01300	14	1·09345
3	1·01950	15	1·10036
4	1·02600	16	1·10750
5	1·03250	17	1·11465
6	1·03916	18	1·12179
7	1·04582	19	1·12894
8	1·05248	20	1·13608
9	1·05914	21	1·14348
10	1·06580	22	1 15088
11	1·07271	23	1·15828
12	1·07962	24	1·16568

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* Mohr, Zeit. Anal. Chem. xii. 137; and Jour. Chem. Soc. 1874, p. 108.

† See also Phillips, Fres. Zeit. 13, 149.

‡ Gerlach, Specifische Gewichte der Salzlösungen, p. 9.

POTASSIUM SULPHATE.

The weighed substance containing no other sulphate is brought into solution, acidified with hydrochloric acid and the sulphuric acid precipitated by decinormal barium chloride. (See Sulphuric Acid.)

c. c. decinormal $BaCl_2 \times \cdot 0039137 = K$
" " " $\times \cdot 0056137 = KOH$
" " " $\times \cdot 0069137 = K_2CO_3$
" " " $\times \cdot 0087137 = K_2SO_4$

Salts of potassium, with the exception of the phosphate borate and silicate, may be converted into sulphate by simply adding an excess of sulphuric acid, evaporating to dryness and igniting in a covered crucible. The ignition must be carefully performed, otherwise loss from decrepitation ensues. The sulphate as first obtained contains an excess of sulphuric acid, and this must be expelled by adding a small fragment of ammonium carbonate and heating to redness. The sulphate, when dissolved in water, must be neutral to litmus paper.

Specific gravity of solutions of Potassium Sulphate at 15°. *Water at* 15° = 1.

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00820	6	1·04947
2	1·01635	7	1·05790
3	1·02450	8	1·06644
4	1·03277	9	1·07499
5	1·04105		

ESTIMATION OF POTASSIUM AS ACID TARTRATE.*

About 1 gm. of the potassium compound, either chloride sulphate or nitrate, is dissolved in water in a beaker which is graduated upon the side. Two gms. of sodium acetate are added and dissolved, and then 2 gms. of tartaric acid dissolved in a small quantity of water. Note the total volume of liquid, and after the deposition of acid tartrate add about $\frac{1}{10}$ as much of 95 % alcohol, when a further deposition takes place. Afterwards the remaining quantity of alcohol is added, which must be such that the total volume of alcohol is double that of the original aqueous solution. After the deposition of crystals has stopped, the contents of the beaker are thrown on a filter and washed with 60 % alcohol until the filtrate no longer reddens blue litmus paper. The filter and contained precipitate are then placed in the beaker in which the precipitation was performed, water added, the liquid heated, litmus added and normal alkali run in until the litmus shows the violet tint.

c. c. normal alkali × ·039137 = K
“ “ “ × ·056137 = KOH
“ “ “ × ·069137 = K_2CO_3
“ “ “ × ·087137 = K_2SO_4
“ “ “ × ·101181 = KNO_3
“ “ “ × ·074594 = KCl

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* Casamajor. Proceed. Amer. Chem. Soc. vol. i. p. 98 ; Am. Chem. 1876, p. 83.

ESTIMATION OF POTASSIUM AND SODIUM AS SILICO-FLUORIDES.*

When hydrofluosilicic acid or a silicofluoride is added to the solution of a potassium or sodium salt, a precipitate of potassium or sodium silicofluoride is formed. If an equal volume of strong alcohol is added to the solution, the precipitation is complete. The precipitate (K_2SiF_6 or Na_2SiF_6) is slightly soluble in water, has an acid reaction to litmus, and is decomposed by sodium or potassium hydrate, silica and sodium or potassium fluoride being formed. $K_2SiF_6 + 4KOH = 6KF + SiO_2 + 2H_2O$. Upon these facts, Stolba has founded a process for the estimation of these metals. The process is most valuable where only one metal is present. Both metals may, however, be estimated by this method, and the potassium estimated in another portion as acid tartrate, and subtracted.

Preparation of Calcium Silicofluoride.—Equal parts of powdered fluor-spar and powdered glass are introduced in a flask provided with funnel and delivery tubes, and a quantity of strong sulphuric acid is added through the funnel tube. Silicon tetrafluoride is evolved and conducted into water by which it is decomposed, silica and hydrofluosilicic acids being formed. $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$. To prevent the delivery tube from being stopped up by the deposited silica, the point dips below the surface of a little mercury in the bottom of the cylinder containing the water. After the gas has passed for some time, the liquid becomes gelatinous from separated silica. It is strained through clean linen, filtered, and saturated with calcium carbonate.*

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* Stolba, Jour. für Prak. Chemie, 89, 129; 94, 24; Fres. Zeit. 3, 298.

The Analysis.—To the solution of the potassium or sodium salt, which must contain no free mineral acid (if free mineral acid be present, a corresponding quantity of calcium acetate must first be added), and must be dissolved in a small quantity of water, an excess of calcium silicofluoride and an equal bulk of strong alcohol are added. The solution, after standing for several hours, is filtered from the nearly transparent precipitate, which is washed with a mixture of one volume alcohol and one volume water, until the washings give no further turbidity with a solution of a potassium salt. The precipitate with the filter is transferred to the beaker in which the precipitation was made, water and litmus added, and the mixture titrated with normal alkali. The alkaline silicofluoride dissolves slowly in water, and the litmus, after being turned blue by the normal alkali, is again reddened if allowed to stand for a time. Normal alkali must be added, therefore, until the blue color remains after standing for some time. The separated silica does not interfere.

c. c. normal alkali × ·019568 = K
“ “ “ × ·023568 = K_2O
“ “ “ × ·011521 = Na
“ “ “ × ·015521 = Na_2O

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* Upon the preparation of hydrofluosilicic acid, see Stolba, Fres. Zeit.

SODIUM.

THE analysis of sodium compounds by the volumetric method is almost identical with that of the potassium compounds.

SODIUM HYDRATE.

Proceed as under Potassium Hydrate.

c. c. normal acid × ·023043 = Na
" " " × ·031043 = Na_2O
" " " × ·040043 = NaOH

TABLE.

Showing the Sodium Oxide (Na_2O) in Soda Lyes of different specific gravities. Temp. 17·5° *

Na_2O per cent.	Specific Gravity.	Na_2O per cent.	Specific Gravity.	Na_2O per cent.	Specific Gravity.	Na_2O per cent.	Specific Gravity.
35·0	1·500	27·5	1·389	20·0	1·281	12·5	1·174
34·5	1·492	27·0	1·382	19·5	1·274	12·0	1·167
34·0	1·485	26·5	1·375	19·0	1·266	11·5	1·160
33·5	1·477	26·0	1·367	18·5	1·259	11·0	1·153
33·0	1·470	25·5	1·360	18·0	1·252	10·5	1·146
32·5	1·463	25·0	1·353	17·5	1·245	10·0	1·139
32·0	1·455	24·5	1·345	17·0	1·238	9·5	1·132
31·5	1·448	24·0	1·338	16·5	1·231	9·0	1·125
31·0	1·440	23·5	1·331	16·0	1·224	8·5	1·118
30·5	1·433	23·0	1·324	15·5	1·217	8·0	1·111
30·0	1·426	22·5	1·317	15·0	1·210	7·5	1·104
29·5	1·418	22·0	1·309	14·5	1·203	7·0	1·097
29·0	1·411	21·5	1·302	14·0	1·195	6·5	1·090
28·5	1·404	21·0	1·295	13·5	1·188	6·0	1·083
28·0	1·396	20·5	1·288	13·0	1·181	5·5	1·076

Na_2O : NaOH : : 31·043 : 40·043.

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* Hoffman-Schaedler. Tabellen für Chemiker.

SODIUM CARBONATE.

Proceed as under Potassium Carbonate.

c. c. normal acid × ·023043 = Na
“ “ “ × ·031043 = Na_2O
“ “ “ × ·053043 = Na_2CO_3

Specific gravity of solutions of Sodium Carbonate at 15°. *Water at* 15°=1.*

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·01050	8	1·08430
2	1·02101	9	1·09500
3	1·03151	10	1·10571
4	1·04201	11	1·11655
5	1·05255	12	1·12740
6	1·06309	13	1·13845
7	1·07369	14	1·14950

SODIUM CHLORIDE.

Proceed as under Potassium Chloride.

c. c. $\frac{n}{10}$ silver solution × ·0023043 = Na
“ “ “ “ × ·0031043 = Na_2O
“ “ “ “ × ·0053043 = Na_2CO_3
“ “ “ “ × ·00585 = NaCl

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* Gerlach, Specifische Gewichte der Salzlösungen.

Specific gravity of solutions of Sodium Chloride at 15°. *Water at* 15°=1. *

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00725	14	1·10384
2	1·01450	15	1·11146
3	1·02174	16	1·11938
4	1·02899	17	1·12730
5	1·03624	18	1·13523
6	1·04366	19	1·14315
7	1·05108	20	1·15107
8	1·05851	21	1·15931
9	1·06593	22	1·16755
10	1·07335	23	1·17580
11	1·08097	24	1·18404
12	1·08859	25	1·19228
13	1·09622	26	1·20098

When potassium and sodium chlorides occur together in solution, which very often happens, the amount of each may be estimated indirectly as follows:

Evaporate the mixed chlorides to dryness, heat nearly but not quite to redness, and weigh them; then dissolve in water and estimate the amount of chlorine by $\frac{n}{10}$ silver solution. The following formula then gives the amounts of sodium and potassium in the mixed chlorides.

$$\left.\begin{aligned} x &= \frac{[(s-a)\,1{\cdot}54]-a}{0{\cdot}63} \\ y &= \frac{a-[(s-a)\,0{\cdot}91]}{0{\cdot}63} \end{aligned}\right\} \begin{aligned} x &= \text{potassium.} \\ y &= \text{sodium.} \\ s &= \text{weight of the chlorides.} \\ a &= \text{`` \quad `` \quad chlorine.} \end{aligned}$$

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* **Gerlach, Specifische Gewichte der Salzlösungen.**

$$1 \cdot 54 = \frac{Cl}{Na}$$

$$0 \cdot 91 = \frac{Cl}{K}$$

$$0 \cdot 63 = \frac{Cl}{Na} - \frac{Cl}{K}$$

Or the following, taken from Fresenius:

Multiply the quantity of chlorine in the mixture by 2·1029, deduct from the product the sum of the chlorides, and multiply the remainder by 3·6288; the product expresses the quantity of sodium chloride contained in the mixed chlorides. To be of any value, the determination of mixed chlorides and of the chlorine must be very accurately made, as small mistakes are multiplied in the calculation. Unless the amounts of potassium and sodium present are nearly equal (not more than two parts of one to one part of the other) the method cannot be depended upon.

Sodium nitrate or chloride may be converted into carbonate by adding to their aqueous solution perfectly pure oxalic acid in moderate excess, and evaporating several times to dryness, with repeated renewal of the water. All the nitric acid of the sodium nitrate escapes in this process (partly decomposed, partly undecomposed); and equally so all the hydrochloric acid in the case of sodium chloride. If the residue is now ignited until the excess of oxalic acid is removed, sodium carbonate is left (Fresenius). The sodium carbonate may be ·termined by standard acid, and from the amount the amount of sodium salt calculated.

SODIUM SULPHATE.

Proceed as under Potassium Sulphate.

c. c. $\frac{n}{10}$ barium chloride × ·0023043 = Na
" " " " × ·0071043 = Na_2SO_4

Specific gravity of solutions of Sodium Sulphate at 15°. *Water at* 15° = 1.*

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00911	7	1·06437
2	1·01822	8	1·07375
3	1·02736	9	1·08325
4	1·03650	10	1·09275
5	1·04575	11	1·10246
6	1·05500		

When potassium and sodium sulphates occur together, the proportion of each may be estimated as follows :

Evaporate to dryness, heat to redness, and weigh the mixed sulphates, then dissolve in water and estimate the amount of SO_4 by means of $\frac{n}{10}$ barium chloride ; then, from the amount of SO_4 found, subtract the weight of the mixed sulphates multiplied by ·551, and divide the remainder by ·125. The quotient is the sodium sulphate.

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* Gerlach, Specifische Gewichte der Salzlösungen.

SODA ASH.

Soda ash made by Leblanc's process contains, besides sodium carbonate, moisture, sodium hydrate, sulphate chloride, silicate, aluminate, and sometimes sulphite, sulphide, and thiosulphate.

Moisture.

About 10 gms. of the sample is heated in a weighed platinum crucible until it ceases to lose weight, cooled in the desiccator, and quickly weighed. The loss is moisture.

Sodium Carbonate and Hydrate.

The cooled mass is dissolved in a small quantity of hot water in a beaker, and filtered into a half litre flask. The filter is thoroughly washed out, and the fluid in the flask, after cooling, diluted to the containing mark, shaken, 15 c. c. taken out, and titrated with normal sulphuric acid. The normal acid used is equal to the combined hydrate and carbonate in 1 gm. of the soda ash.

Take out another 50 c. c. of the solution, pour into a flask, add an excess of barium chloride to the boiling solution, filter and wash rapidly into another flask, and titrate the filtrate with normal acid. Or, the estimation may be made by taking out 100 c. c. and titrating. In either case a slight error is introduced. In the first case, because the filter paper retains a little of the barium hydrate, and in the second, from neglecting the volume of the precipitated barium carbonate. The c. c. of normal acid used × ·031043 = Na_2O, and subtracted from the amount used for the total alkali = c. c. equivalent to sodium carbonate. This number is then to be multiplied by ·053043 for anhydrous sodium carbonate.

SULPHURIC ACID

is estimated by slightly acidifying 50 c. c. of the solution with HCl, and precipitating with decinormal barium chloride.

HYDROCHLORIC ACID.

Neutralize 50 c. c. with nitric acid free from chlorine, boil to expel H_2S, and then add a drop or two of a solution of pure sodium carbonate until faintly alkaline, add two drops saturated solution of potassium chromate, and run in $\frac{n}{10}$ silver nitrate until the brick red color is persistent.

SULPHIDE AND THIOSULPHATE.

50 c. c. of the solution are diluted considerably, acidified slightly with acetic acid, starch added, and $\frac{n}{10}$ iodine run in until the blue color remains. The c. c. used = combined sulphide and thiosulphate. A second portion of 50 c. c. is precipitated with a solution of zinc sulphate, and the filtrate containing only this sulphate titrated as above. The difference between the first and second results is equal to the thiosulphate.

Potash or crude potassium carbonate may be estimated in the same way as soda ash. Potash always contains more or less sodium carbonate, which is sometimes added as an adulterant: being less valuable than potassium carbonate. The amount of each contained in potash may be determined by the following method:* Dissolve 6·25 gms. of the gently ignited pearlash in water, filter the solution into a quarter-litre flask, add acetic acid in slight excess, apply a gentle heat until the carbonic acid is expelled, then add to the fluid, while still hot, acetate of lead, drop by drop, until the formation of a precipitate of sulphate of lead *just* ceases. Allow the mixture to cool, add water up to the mark, shake, allow to deposit, filter through a dry filter, and transfer 200 c. c. of the filtrate, corresponding to 5 gms. of pearlash, to a quarter-litre flask. Add sulphuretted hydrogen water up to the mark, and shake. If the acetate of lead has been carefully added, the fluid will now smell of sulphuretted hydrogen, and no longer contain lead; in the contrary case, sulphuretted hydrogen gas must be conducted into it. After the sulphide of lead has subsided, filter through a dry filter, evaporate 50 c. c. of the filtrate (corresponding to 1 gm. of pearlash), with addition of 10 c. c. hydrochloric acid of 1·10 sp. gr. in a weighed platinum dish, to dryness; then cover the dish, heat, and weigh; the weight found expresses the total quantity of chloride of potassium and chloride of sodium given by 1 gm. of the pearlash. Estimate the potassa and soda now severally in the indirect way, by determining the chlorine volumetrically. (See Chlorine.) The potassa may also be determined directly by precipitation as tartrate. (See page 72.)

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* Fresenius, Quant. Analysis.

BARIUM.

Barium Oxide and Hydrate.

Dissolve the substance in water, add litmus, and titrate with normal acid.

c. c. normal acid × ·0685 = Ba
" " " × ·0855 = $Ba(OH)_2$

Barium Carbonate.

Weigh out about ·2 gms. substance, dissolve in a measured excess normal HCl, boil, add litmus, and then run in standard sodium hydrate from a second burette until the blue color is restored. The c. c. of acid — the c.c. of standard sodium hydrate (if both solutions be strictly normal) = the number of c. c. of acid required to saturate the barium carbonate.

c. c. normal acid × ·0685 = Ba
" " " × ·0855 = $Ba(OH)_2$
" " " × ·0985 = $BaCO_3$

The carbonic acid in barium carbonate may likewise be determined by one of the methods given under carbonic acid, and the barium calculated from the carbonic acid found.

$$CO_2 \times 3{\cdot}11363 = Ba$$
$$CO_2 \times 4{\cdot}47727 = Ba_2CO_3$$

BARIUM CHLORIDE.

All other chlorides must be absent. Determine the chlorine as in the case of potassium chloride, having first precipitated the barium from the chloride by means of a solution of K_2SO_4.

c. c. $\frac{n}{10}$ silver solution $\times \cdot 00685 = Ba$
“ “ “ “ $\times \cdot 00855 = Ba(OH)_2$
“ “ “ “ $\times \cdot 00985 = BaCO_3$
“ “ “ “ $\times \cdot 01039 = BaCl_2$

DETERMINATION OF BARIUM AS OXALATE.*

The solution containing the barium is mixed with an excess of a concentrated solution of oxalic acid, and an equal volume of alcohol added. After standing over night, the solution is filtered, the precipitate washed with alcohol until the filtrate no longer reddens blue litmus paper, and then carefully dried in the air-bath to expel the alcohol. The precipitate is dissolved in the smallest possible quantity of hydrochloric acid, diluted with water, and permanganate run in until it communicates a faint permanent pinkish tint to the liquid.

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* Leison, Chem. News, xxii. 210; Amer. Jour. Sci., Sept. 1870.

c. c. $\frac{n}{10}$ permanganate × ·00685 = Ba
" " " × ·00765 = BaO
" " " × ·01039 = $BaCl_2$

BY PRECIPITATION AS CHROMATE.

The neutral or slightly ammoniacal solution is treated with potassium chromate in slight excess at the boiling temperature, by which the barium is completely precipitated as chromate. It is filtered, washed with hot water until the filtrate is entirely colorless, and while still moist pushed together with the filter in the stoppered bottle, Fig. 30, some hydrochloric acid is added, and then the air of the flask is displaced by carbon dioxide. This is most easily accomplished by throwing in a crystal of sodium bicarbonate. As soon as it is all dissolved and effervescence ceases, add an excess of potassium iodide to the solution, insert the stopper of the bottle and fasten it securely in the frame. The bottle is then placed in water, which is heated for some time. After the reaction is completed, the bottle is allowed to cool, opened, and the free iodine found by adding starch solution and running in decinormal sodium thiosulphate until the blue color disappears.

The reaction between the barium chromate, potassium iodide, and hydrochloric acid is as follows:

$$2BaCrO_4 + 6KI + 16HCl = 2BaCl_2 + Cr_2Cl_6 + 6KCl + 6I + 8H_2O$$

$$\text{Since } 2BaCrO_4 = 6I$$

$$\frac{BaCrO_4}{3} = I$$

and $\frac{1}{8}$ atom of Ba, or 45·66, would correspond to a normal solution of iodine, 4·566 to a decinormal, and ·004566 to 1 c. c. of a decinormal solution. Since the decinormal sodium thiosulphate is equivalent to decinormal iodine,

c. c. $\frac{n}{10}$ sodium thiosulphate × ·004566 = Ba
" " " " × ·0051 = Ba

ESTIMATION WITH STANDARD POTASSIUM BICHROMATE.

Preparation of the Solution of Bichromate.—This solution is not identical with the one described on page 49, and must not be confounded with it; that being used for oxidation, while this is for precipitation. It is made by dissolving 7·3808 gms. pure potassium bichromate (previously heated nearly to fusion, to drive off hygroscopic moisture) in water, and diluting to a litre.

The barium solution is made alkaline by addition of ammonia free from carbonic acid and heated nearly to boiling. The bichromate solution is then added slowly, allowing to settle after each addition until the supernatant fluid shows a slight yellow tint. A very small excess of the bichromate shows in the alkaline liquid, and with care the results are tolerably sharp.

Lead must be absent as well as all metals which form chromates insoluble in ammoniacal solution. Calcium and small quantities of strontium exercise no influence upon the result.

c. c. decinormal bichromate × ·00685 = Ba
" " " × ·00765 = BaO

Barium may also be precipitated as chromate, washed, the precipitate dissolved in a little HCl, and the barium precipitated by H_2SO_4. Without filtering, some starch paste and a little KI are added to the solution, and $\frac{n}{10}$ stannous chloride run in until the blue color disappears.* Or,

An excess of $\frac{n}{10}$ potassium bichromate is added to a slightly alkaline solution of the barium compound, the precipitate filtered and washed, and the excess of chromic acid in the filtrate determined by one of the methods given under Chromium.

PRECIPITATION OF BARIUM AS SULPHATE IN ACID SOLUTION.

Lead and strontium must first be removed.

This method possesses the very great advantage that it is applicable to the estimation of all compounds of barium without exception, and that it may be used in presence of all metals except lead and strontium.

We need decinormal solutions of barium chloride and sulphuric acid.

Weigh out 12·1958 gms. pure dry barium chloride, dissolve in water and make up to a litre. If it be desired to have a control upon this solution, 20 c. c. may be measured out, slightly acidified with hydrochloric acid, and the barium precipitated by an excess of dilute sulphuric acid, and weighed.

The solution of sulphuric acid is made by dissolving 3 c. c. of the concentrated acid in water, allowing the solution to cool, diluting to about 500 c. c., determining the exact strength by taking 10 c. c. and titrating by $\frac{n}{10}$ barium chloride, and then running a sufficient quantity into a litre flask to make the solution of precisely decinormal strength when diluted to a litre. Suppose for 10 c. c. of an acid made according to the above directions, 20·8 c. c. decinormal barium chloride are required, then $\frac{10}{20.8} \times 1000$ or 480·8 c. c., is the amount required per litre. As a control the amount of acid may also be determined by precipitating 20 c. c. by an excess of barium chloride. Having prepared decinormal solutions, it is easy to make the analysis. For this purpose, fill two burettes, one with $\frac{n}{10}$ barium chloride, the second with $\frac{n}{10}$ sulphuric acid. Weigh out the substance to be tested, dissolve in water, wash into the 300 c. c. flask, fill to the mark, and take out 50 or 100 c. c. with a pipette. Acidify *slightly* with hydrochloric acid, and then run in 10 c. c. of the sulphuric acid. Heat to boiling for a few minutes, and then take out a portion of the liquid by means of the filtering pipette, Fig. 33, and add a drop of the sulphuric acid from the burette. If a precipitate is formed, rinse the pipette and tube into the beaker and add another 10 c. c. of acid. As soon as no precipitate is formed in the clear fluid taken out with the pipette, the sulphuric acid is in excess, 1 c. c. of barium chloride is then added, and the fluid tested by a drop of the sulphuric acid. If sufficient has not been added, more is run in. When the barium is again in excess, the sulphuric acid is run in by portions of ·2 c. c., finally ·1 c. c., until a portion of the filtrate gives no precipitate with a drop of sulphuric acid at first, but the liquid becomes turbid in a few seconds. A portion of the liquid is then run into a second test tube and a drop of the barium chloride added. If this also produces a turbidity after the lapse of a few seconds, the proper point is reached. Subtract, now, the c. c. of barium chloride used from the c. c. of sulphuric acid, and the remainder will be the sulphuric acid required for the barium originally in the solution. Now take out a second portion of the solution from the flask, and, knowing the amount required, run in nearly the entire number of c.c. at first, and then by ·1 c. c. until the proper point is reached. After a little practice, very little time is required to hit the precise point when the reaction is completed, as from the amount of precipitate produced in the test tube a tolerably good idea of the acid still necessary can be formed. The method gives excellent results.

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* See Hinman, Amer. Jour. Sci. 1877, p. 478.

c. c. decinormal $H_2SO_4 \times \cdot 00685 = Ba$
" " " $\times \cdot 00765 = BaO$

Barium sulphate may be estimated by fusion with a mixture of potassium and sodium carbonates, whereby the acids exchange places, and potassium and sodium sulphates and barium carbonate are formed. The fused mass is treated with hot water, which leaves the barium carbonate undissolved; this is washed, dissolved in an excess of normal or decinormal hydrochloric acid, and the excess found by standard alkali.

STRONTIUM.

STRONTIUM OXIDE AND HYDRATE.

DETERMINED like Barium Hydrate.

c. c. decinormal acid × ·004377 = Sr
“ “ “ × ·006077 = $Sr(OH)_2$

STRONTIUM CARBONATE.

Determined like Barium Carbonate.

c. c. decinormal acid × ·004377 = Sr
“ “ “ × ·006077 = $Sr(OH)_2$
“ “ “ × ·007377 = $SrCO_3$

STRONTIUM CHLORIDE.

First precipitate the strontium by means of a solution of potassium sulphate, and determine the chlorine in the filtrate with $\frac{n}{10}$ silver solution.

c. c. decinormal silver solution × ·00437 = Sr
“ “ “ “ × ·00792 = $SrCl_2$

ESTIMATION AS OXALATE.*

In the absence of barium, calcium, and other metals ipitable as oxalates, a strong solution of oxalic added in excess, and then a volume of strong alcohol equal to the amount of liquid. The solution is allowed to stand over night, and filtered through a sand filter made by dropping a bulb of glass blown upon the end of a small tube into the neck of a funnel, and filling clean sand around it. The bulb closes the funnel sufficiently to prevent the passage of the sand, but not the liquid. The precipitate is dried thoroughly to expel all alcohol, the bulb lifted by means of the glass stem, and the sand and precipitate washed into a beaker below, hot dilute sulphuric acid added to decompose the oxalate, and, after dilution with water, titrated with $\frac{n}{10}$ permanganate. Instead of the sand filter a funnel may be used which has a quantity of fine asbestos placed in the neck.

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* Leison, Chem. News, xxii. 210.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 004377 = Sr$
" " " $\times \cdot 005177 = SrO$

The method used for barium, namely, precipitation as sulphate, may also be used with strontium, but is not so good, since the strontium sulphate is slightly soluble in water and dilute acid.

CALCIUM.

Calcium Hydrate, or Oxide.

Calcium hydrate is less soluble in water than either barium or strontium hydrate, and a modification of the method is hence necessary. The best plan is to dissolve the weighed substance in excess of normal or decinormal acid, and estimate the excess of acid by means of standard sodium hydrate.

c. c. normal acid × ·020 = Ca
“ “ “ × ·037 = $Ca(OH)_2$
“ “ “ × ·028 = CaO

Calcium Carbonate.

Determined like the Hydrate.

c. c. normal acid × ·020 = Ca
“ “ “ × ·037 = $Ca(OH)_2$
“ “ “ × ·028 = CaO
“ “ “ × ·050 = $CaCO_3$

Where calcium oxide or hydrate and carbonate occur together, the amount of carbonate may be determined by estimating the amount of CO_2 present, by one of the methods given under Carbonic Acid, and the amount of calcium existing as carbonate calculated from this. Then subtracting this from the total Ca present, we have remaining that existing as CaO or $Ca(OH)_2$.

Calcium Chloride.

Evaporate to hard dryness, heat to 200° in the air-bath, dissolve in water, and determine the chlorine with $\frac{n}{10}$ silver solution.

c. c. $\frac{n}{10}$ silver solution × ·0020 = Ca
“ “ “ “ × ·0037 = $Ca(OH)_2$

c. c. $\frac{n}{10}$ silver solution × ·0028 = CaO
" " " " × ·0050 = $CaCO_3$
" " " " × ·00555 = $CaCl_2$

Calcium Sulphate.

Dissolve in sufficient water and some dilute HCl, and determine the sulphuric acid by decinormal barium chloride.

c. c. $\frac{n}{10}$ barium chloride × ·0020 = Ca
" " " " × ·0050 = $CaCO_3$
" " " " × ·00555 = $CaCl_2$
" " " " × ·0068 = $CaSO_4$

ESTIMATION AS OXALATE.

Any calcium salt soluble in water, or dilute acetic acid.

1. Dissolve in water and add ammonium hydrate until the fluid is alkaline, and then ammonium chloride and oxalate. Heat gently until the calcium oxalate has completely separated, collect on a filter, wash thoroughly, dissolve in warm dilute sulphuric acid, and estimate the oxalic acid by $\frac{n}{10}$ permanganate. In case the calcium salt be insoluble in water but soluble in dilute acetic acid, it is to be dissolved in the smallest possible quantity of acetic acid, and the calcium precipitated as oxalate without previous addition of ammonium hydrate.

2. Add to the solution of the calcium salt, in a 250 c. c. flask, a known volume in excess of a solu-

tion of ammonium oxalate. Fill the flask to the mark with water, allow the precipitate to subside, take out 50 or 100 c. c. by means of a pipette, and determine the excess of oxalic acid by acidifying with sulphuric acid, and titrating with $\frac{n}{10}$ permanganate.

3. Collect the precipitate of calcium oxalate on a filter, dry the filter, and ignite; in this way the oxalate is converted into a mixture of carbonate and oxide, dissolve in excess of decinormal acid, and measure the excess with decinormal sodium hydrate. The difference is the measure of acid required. All three of these methods give good results.

c. c. $\frac{n}{10}$ permanganate or acid × ·0020 = Ca
“ “ “ “ × ·0050 = $CaCO_3$
“ “ “ “ × ·0028 = CaO

MAGNESIUM.

Magnesium Oxide.

Dissolve in excess of normal acid, and estimate the excess with Kieffer's Solution. (See page 40.)

Magnesium Carbonate.

Dissolve in excess of normal acid, and titrate back with Kieffer's Solution.

c.c. normal acid × ·0120 = Mg
“ “ “ × ·0200 = MgO
“ “ “ × ·0420 = $MgCO_3$

These estimations are generally of little value.

MAGNESIUM SULPHATE.

Most magnesium compounds may be converted into the sulphate by evaporating to dryness with concentrated sulphuric acid, and heating to very dull redness to drive off the excess. The heat must not be greater than low redness, otherwise some of the sulphate is apt to be decomposed. Dissolve the sulphate in water, add a few drops of hydrochloric acid and determine the sulphuric acid by means of decinormal barium chloride. (See Sulphuric Acid.)

c. c. $\frac{n}{10}$ barium chloride × ·0012 = Mg
“ “ “ “ × ·0020 = MgO
“ “ “ “ × ·0042 = $MgCO_3$
“ “ “ “ × ·0060 = $MgSO_4$

ESTIMATION AS PHOSPHATE.

The solution must be free from other metals except potassium and sodium. Ammonium chloride and ammonia are added, and then sodium phosphate in excess. The solution is allowed to stand for twelve hours, then filtered and washed with a solution made by mixing three parts water and one part ammonia, sp. gr. 0·96, until the filtrate produces only a very faint opalescence when mixed with nitric acid in excess, and a drop of silver nitrate solution added. (Fresenius.)

1. The precipitate is then dissolved in acetic acid, and the amount of phosphoric acid estimated by titration with uranium solution. (See Phosphoric Acid.)

c. c. uranium solution × ·001695 = Mg
" " " × ·002817 = MgO

2. Magnesium ammonium phosphate, when dissolved in water, in which it is slightly soluble, has an alkaline reaction to cochineal. If hydrochloric acid is added, the alkaline reaction is destroyed, when all the magnesium is converted into chloride.

$$MgNH_4PO_4 + 2HCl = MgCl_2 + NH_4H_2PO_4$$

The magnesia is precipitated as before directed and washed with ammoniacal water, then with ordinary alcohol of neutral reaction, until the filtrate no longer changes red litmus to blue. The precipitate and filter are placed in the same beaker in which the precipitation was made, water and a few drops of cochineal solution added, and normal or decinormal acid run in until the violet color changes to yellow.*

c. c. normal acid × ·012 = Mg
" " " × ·020 = MgO

[illegible], Fres. Zeit. 16, 100 ; see also Mohr, ibid. 326.

ESTIMATION AS OXALATE.*

When oxalic acid is added in excess to magnesium sulphate, the mixture evaporated (but not to dryness), and alcohol added, the filtrate is perfectly free from magnesium. The precipitate is brought upon a filter washed with alcohol, and dried carefully to expel the alcohol, the oxalate is then dissolved in sulphuric acid, and determined by $\frac{n}{10}$ permanganate.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 0012 = Mg$
" " " $\times \cdot 0020 = MgO$

ZINC.

Zinc Oxide and Carbonate.

Estimated with normal acid in excess, and titrating back with Kieffer's Solution. The estimation is not accurate with small amounts of substance.

c. c. normal acid $\times \cdot 03258 = Zn$
" " " $\times \cdot 04058 = ZnO$

Zinc Oxalate.†

The solution containing the zinc, preferably as sulphate, must be neutral. Add an excess of a strong solution of oxalic acid, and then a volume of strong alcohol equal in bulk to that of the solution containing the zinc Allow the solution to stand over night, filter off the zinc oxalate formed, through a funnel in the neck of which is placed a loosely-fitting plug of fine asbestos, and wash with alcohol. *Dry perfectly in the air-bath*, take out the asbestos plug, and place in hot dilute sulphuric acid, by which the oxalate is dissolved, wash out the oxalate adhering to the funnel into the same beaker, with a little of the dilute sulphuric acid, and titrate with $\frac{n}{10}$ permanganate. The asbestos does not interfere in the slightest degree.

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* Leison, Chemical News, xxii. 210.

† Ibid.

c. c. $\frac{n}{10}$ permanganate × ·003258 = Zn
" " " × ·004058 = ZnO
" " " × ·008058 = $ZnSO_4$

ESTIMATION AS SULPHIDE.

Applicable to any soluble zinc salt.

The solution in a flask is made just alkaline by addition of sodium or ammonium hydrate, sodium or ammonium sulphide in excess added, the flask filled with warm distilled water, tightly corked or stoppered, and allowed to stand in a warm place for several hours. A tube drawn out at one end and containing a loosely-fitting plug of fine asbestos,
then arranged as in Fig. 34. The bent tube is
cted with a Bunsen pump. After the liquid
he precipitate in the flask has become per-
nd the precipitate settled, pour the clear
the asbestos filter. As soon as the

fluid has run through, close the tube with a
cork, fill the flask with warm, recently-boiled
containing a little am-
um hydrate, cork tight-
nd allow the flask to
until the precipitate
subsides; then pour
lear fluid upon the fil-
and repeat this three
ur times; finally, wash
of the precipitate upon
sbestos filter, and wash
lly with warm water con-
ng ammonia until a drop
e filtrate produces no
precipitate in an alka-
ead solution. Then re-
the tube containing the
stos and zinc sulphide
the Woulfe's bottle, and by means of a stiff
inserted at the small end, force the asbestos
zinc sulphide into the flask in which the precipi-
n was made, wash any zinc sulphide still adher-
o the tube into the flask, and add a quantity
n acid solution of ferric sulphate more than
ient to decompose the zinc sulphide. Stopper
flask securely, and allow to stand in a warm
, shaking occasionally. The reaction which
place may be represented thus:

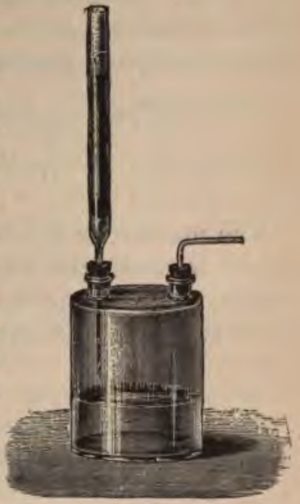

FIG. 34.

$$Fe_2(SO_4)_3 + ZnS = 2FeSO_4 + ZnSO_4 + S$$

the reaction is completed, the solution should
ss a yellow color due to undecomposed ferric

191955A

salt. The stopper of the flask is now removed, when no smell of sulphydric acid should be perceptible, and the solution diluted and titrated with $\frac{n}{10}$ permanganate. If the solution be dilute, the finely divided sulphur present does not interfere.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 003258 = Zn$
" " " $\times \cdot 004058 = ZnO$
" " " $\times \cdot 008058 = ZnSO_4$

The method is a tolerably good one when care is taken to wash the zinc sulphide rapidly and thoroughly. Owing to its slimy nature, this is, however, somewhat difficult to accomplish.

PRECIPITATION AS SULPHIDE WITH ALKALINE LEAD SOLUTION AS INDICATOR.

We need standard solutions of zinc sulphate and sodium sulphide and an alkaline lead solution.

Standard Zinc Solution.—Made by dissolving 44·7 gms. pure zinc sulphate ($ZnSO_4 + 7H_2O$) in water and diluting to a litre. Instead of this salt we may use 68·2066 gms. double sulphate of zinc and potassium, prepared by mixing hot solutions of the two salts in the proportions of their molecular weights, and allowing to crystallize. Such a solution contains ·0100 gms. zinc per c. c., which in this case is more convenient for purposes of calculation than a decinormal solution.

Standard Sodium Sulphide is prepared by passing sulphydric acid into a solution of sodium hydrate of sp. gr. ·094 until saturated, adding sodium hydrate until the solution no longer smells of H_2S, and diluting with water until it nearly corresponds in strength to the standard zinc solution. It is not necessary that the solutions be precisely equivalent, since the sodium sulphide decomposes slowly, and its strength must be determined before each series of analyses by means of the zinc solution.

Alkaline Lead Solution.—Made by adding some tartaric acid to a solution of sodium hydrate, and pouring this into a solution of lead acetate until the precipitate at first formed is redissolved.

Numerous substitutes have been proposed for the alkaline lead solution, sodium nitro-prusside, and nickelous and cobaltous chlorides among the number, but they possess no advantage over the lead solution and are more expensive. Ferric chloride, which is often used, is not sufficiently sensitive.

Determination of the Relative Strength of the Solutions.—Take out 20 c. c. of the zinc solution and add the sodium sulphide from a burette, stirring after each addition. From time to time a drop of the alkaline lead solution is taken out from a bottle containing it, by means of a glass rod, and placed upon a piece of fine white filtering paper, and near it, upon the same piece of paper, a drop of the turbid zinc solution. The liquids spread over the paper and run into each other, and as soon as an excess of sodium sulphide is present show a dark line where the drops meet. Placing the drops upon filter paper is absolutely necessary, since if a porcelain plate were used, the alkaline lead solution would come in contact with the zinc sulphide, which blackens it, producing the same appearance as if sodium sulphide were in excess. The lead solution must be dropped on the paper first, and the drop of turbid fluid then placed beside it.

A notable excess of sodium sulphide must be used before the lead solution shows its presence, and this amount in excess increases with the volume of the liquid used. For this reason a correction must be applied in every case, and this is done as follows: After the zinc is all precipitated and sodium sulphide is in slight excess, the whole solution is poured into a measuring jar and the volume of liquid found roughly. The same volume of water is then taken, and sodium sulphide added, drop by drop, until a drop taken out gives the dark line with alkaline lead solution. The amount used for this purpose is then subtracted from that used for the analysis, and the remainder is the amount to which the 20 c. c. of zinc solution are equivalent.

Suppose that 20 c. c. of the zinc solution required 20·5 c. c. sodium sulphide, the volume of liquid in the beaker is then 40·5 c. c. A like volume of water requires ·2 c. c. sodium sulphide, then 20·5 c. c. − 2 c. c. = 20·3 c. c. is the volume of sodium sulphide equal to 20 c. c. zinc solution. The 20 c. c. contain 20 × ·01 = ·20 zinc, and since this is the amount to which 20·3 c. c. are equivalent, ·1 c. c. sodium sulphide $= \frac{\cdot 20}{20 \cdot 3} =$ ·009852 Zn.

The analysis is performed with two burettes: one containing the zinc solution, the other the sodium sulphide. The sulphide is added until the lead indicator shows it to be in excess. If this point is overstepped in the first trial, which may easily happen, a few c. c. of zinc solution may be added, and the titration again proceeded with. After the titration is ended, the volume of liquid is found, and a correction made by adding sodium sulphide to a like volume of water.

Suppose 30·3 c. c. sulphide have been used and the correction found, ·4 c. c. The volume actually needed was then 30·3 c. c. − ·4 c. c. = 29·9 c. c., and this is equal to 29·9 × ·009852 = ·29457 Zn. For the same analysis 4·5 c. c. zinc solution were used, which is equal to ·045 Zn. The substance, therefore, contained ·29457 − ·045 = ·24957 gms. Zn.

The zinc solution to be titrated must be neutral or alkaline.

The method is inapplicable in presence of copper, manganese, nickel, or cobalt.

ESTIMATION AS FERROCYANIDE.*

The zinc must be in slightly acid (preferably hydrochloric) solution, and should contain neither ammonium chloride nor sodium acetate. Copper, iron, nickel, and cobalt must be absent; manganese does not interfere.

Standard Solution of Potassium Ferrocyanide is prepared by dissolving about 43· gms. potassium ferrocyanide in water and diluting to a litre. The strength of this solution is estimated by titrating it against a measured volume of the standard zinc solution.

Standard Zinc Solution.—This is the same as the one used in the estimation of zinc as sulphide, and contains ·01 gms. zinc per c. c.

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* Fahlberg, Zeit. Anal. Chem. 1874, 379; Lyte, Chem. News, xxxiii. 222.

Twenty c. c. of the zinc solution are measured into a beaker and 1 c. c. hydrochloric acid added. The ferrocyanide is then run in from a burette and the solution tested after each addition by taking out a drop and placing it near a drop of dilute solution of ferric chloride upon filter paper. The drops then run together, and as soon as the ferrocyanide is in excess, a blue line is formed at the intersection. An excess, of ferrocyanide is always used, and the amount in excess depends somewhat upon the dilution; it is therefore best to apply a correction for this in the same way as in the estimation of zinc as sulphide. If ammonium chloride is present, a larger amount of ferrocyanide is used, and the results obtained are then of no value unless the amount of ammonium chloride present is the same in every case.

Sodium acetate prevents the ferric chloride from showing an excess of ferrocyanide. If it be present, we must use uranic acetate or nitrate for the indicator as recommended by Fahlberg and Lyte; but even then the amount of sodium acetate must be the same in every case.

The following experiments, in which ferric chloride was used as indicator, show the degree of accuracy which may be expected. The zinc solution used was made decidedly acid by addition of HCl.

'n solu'n	required	8·45 c. c.	ferrocyanide	after	correc'n	= 8·25 c. c.
"	"	8·4 c. c.	"	"	"	= 8·2 c. c.
"	"	16·7 c. c.	"	"	"	= 16·5 c. c.
"	"	16·5 c. c.	"	"	"	= 16·3 c. c.

10 c. c. Zn solution + 2 gms. NH_4Cl = (corrected) 8·5 c. c. ferrocyanide
10 c. c. " " " ". " 8·5 c. c. "
10 c. c. " " + 1 c. c. HCl = " 8·25 c. c. "

ESTIMATION AS FERRICYANIDE.

The zinc must be in acetic acid solution; and if not already so, this may be accomplished by adding sodium acetate in excess to the slightly acid solution by which the mineral acid is saturated, and an equivalent of acetic acid set free. Potassium ferricyanide is then added, until a drop of the solution taken out upon filter paper, gives a blue ring with a drop of ferrous sulphate solution. Potassium iodide is added in excess, and then a few drops of starch and $\frac{n}{10}$ thiosulphate run in until the blue color is discharged. The reaction is as follows:

$$2Zn_3(Cy_6Fe)_2 + 4C_2H_4O_2 + 4KI = 2Zn_2Cy_6Fe + 4KC_2H_3O_2 + H_4Cy_6Fe + I_4$$

ANALYSIS OF ZINC ORES, ZINC BLENDE, ETC.

THE ore is dissolved in hydrochloric acid, if it be a silicate or carbonate, and evaporated to dryness to separate the silica. If the ore is blende, it is dissolved in nitric acid, to which a few crystals of potassium chlorate are added from time to time. The solution is evaporated to dryness, hydrochloric acid added, and again evaporated to drive off nitric acid. The residue is dissolved in a few drops of hydrochloric acid, diluted, and if metals precipitable by H_2S are present, they are removed by passing a stream of that gas through the liquid. To the filtered liquid ammonia is added until a heavy black precipitate is formed, and this is re-dissolved by adding dilute HCl until the liquid is just distinctly acid. Any nickel or cobalt present remains undissolved as black sulphide, and is filtered off and washed. The iron in the filtrate is oxidized by boiling the solution to expel any H_2S remaining, and adding a few drops of nitric acid or some crystals of potassium chlorate. If the zinc is to be estimated as sulphide, manganese as well as iron must be removed, and the solution is treated as follows: It is heated nearly to boiling, and sodium carbonate added until the solution is of dark red color, but without any precipitate; 2 gms. sodium acetate is then added, and the solution covered and boiled for 15 minutes. The precipitate is allowed to settle, washed twice or three times by decantation, re-dissolved in hydrochloric acid, and re-precipitated in the same way. The two filtrates which must be colorless and free from iron, are united and evaporated to a small bulk, bromine is then added, and the solution covered and set aside for four or five hours in a warm place until the excess of bromine is driven off. If the solution has a pink tint, a part of the manganese is converted into permanganic acid. This is destroyed by heating the solution with a few drops of alcohol. The solution is now filtered from the precipitated manganese oxides, and the zinc in the filtrate then determined.

If the zinc is estimated as ferrocyanide, the manganese need not be removed, and the removal of the iron is effected as follows: Oxidize the iron by nitric acid or potassium chlorate as above, and then add ammonia in sufficient quantity to precipitate the iron and zinc, and re-dissolve the zinc. The solution is filtered, the precipitate washed by decantation, re-dissolved in the least possible hydrochloric acid, and again precipitated in the same way. The filtrates are united, evaporated until most of the ammonia is driven off, then an excess of HCl added, and the zinc estimated by potassium ferrocyanide. The object of dissolving the ferric oxide and re-precipitating is to separate the zinc which is at first carried down with it, and which no amount of washing will remove. In re-dissolving, care should be taken not to use a large excess of HCl, as this gives rise to a large amount of ammonium chloride when neutralized, interfering with the accurate estimation of the zinc by potassium ferrocyanide.

CADMIUM.

ESTIMATION AS SULPHIDE.

THE metal is precipitated as sulphide by passing a stream of H_2S through the slightly acid solution. The precipitate is filtered and washed until the filtrate no longer colors solution of lead acetate. The precipitate and filter are placed in the stoppered bottle, Fig. 30, an excess of an acid solution of ferric sulphate added, and the air displaced by dropping in a crystal of sodium bicarbonate. The stopper is inserted, the filter and contents divided by shaking the bottle, which is then placed in water and heated until the decomposition is complete, taken out, allowed to cool, and contents titrated with permanganate. The decomposition is $Fe_2(SO_4)_3 + CdS = 2FeSO_4 + CdSO_4 + S$.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 0056 = \text{Cd}$$

ESTIMATION AS OXALATE.

The process is the same as for zinc. The solution must be free from other metals precipitable as oxalates.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 0056 = \text{Cd}$$

MANGANESE.

MANGANESE OXIDES.

THE oxides of manganese are four in number, and have the following composition:

MnO
Mn_2O_3
Mn_3O_4
MnO_2

The manganous salts are formed by combination of the acids with the first of these oxides.

Besides these, we have two compounds of manganese with oxygen and hydrogen, which act like acids. The potassium salts of these have the composition:

K_2MnO_4 potassium manganate.
$KMnO_4$ " permanganate.

ESTIMATION OF MANGANESE IN MANGANOUS SALTS.

AS MANGANOUS OXALATE.

THE manganese must be in neutral solution; if acid, sodium oxalate may be added in quantity sufficient to satisfy the mineral acid and set free an equivalent of oxalic acid, add oxalic acid in excess, and then an equal volume of alcohol. The solution is allowed to stand over night, filtered through asbestos, washed with alcohol, *dried thoroughly* in the air-bath, dissolved in dilute sulphuric acid, and titrated with permanganate. All other metals precipitable by oxalic acid, calcium, barium, strontium, zinc, lead, nickel, cobalt, etc., must first be removed.

c.c. $\frac{n}{10}$ permanganate $\times \cdot 00275 = Mn$
" " " $\times \cdot 00355 = MnO$
" " " $\times \cdot 00435 = MnO_2$

BY REDUCTION OF POTASSIUM FERRICYANIDE.

When a manganous salt is mixed in the presence of ferric oxide, and at the boiling temperature with an alkaline solution of potassium ferricyanide, the potassium ferricyanide is converted into ferrocyanide, and manganese dioxide is precipitated, $2K_3FeCy_6 + 4KOH + MnSO_4 = 2K_4FeCy_6 + K_2SO_4 + MnO_2 + 2H_2O$. The ferrocyanide formed can then be measured by means of $\frac{n}{10}$ permanganate, and the amount of manganese calculated from this.

Dissolve the manganese salt in water or acid, add a few c. c. of a ferric chloride solution, and pour into a boiling strongly alkaline solution of potassium ferricyanide contained in a flask. After boiling a few minutes, the brownish black precipitate becomes granular and less bulky. Allow to cool completely, pour into a half litre flask, fill to the mark with water, shake, allow the precipitate to settle, take out a portion of the clear fluid with a pipette, acidify with H_2SO_4, and determine the amount of ferrocyanide contained in it by titration with $\frac{n}{10}$ permanganate. A small error is here introduced from neglecting the volume of the precipitate.

If the estimation must be exact, the liquid, after boiling, is filtered into a half litre or litre flask, the precipitate thoroughly washed, the filtrate diluted to the mark with water, shaken, a portion taken out, acidified with sulphuric acid, and titrated.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 00275 = Mn$
" " " $\times \cdot 00355 = MnO$
" " " $\times \cdot 00435 = MnO_2$

Certain precautions suggested by Fresenius should be attended to.

1. There should be present one equivalent of

ferric oxide for every equivalent of manganese, but the ferric oxide should not be largely in excess of this amount.

2. The solution must not be boiled too long, since if potassium ferricyanide be boiled for a long time with potassium hydrate, a portion is converted into ferrocyanide.

3. The potassium hydrate used must be free from organic matter, and should be fused in a silver dish before being used, if there be any doubt upon this point.

4. The precipitate of MnO_2 must be thoroughly washed.

BY DIRECT TITRATION WITH PERMANGANATE.

When permanganate is added to a neutral manganous salt at the temperature of 80°, the following reaction occurs, $2KMnO_4 + 3MnSO_4 + 2H_2O = K_2SO_4 + 5MnO_2 + 2H_2SO_4$.

The solution containing the manganese must be largely diluted, permanganate is added until the liquid above the precipitate which forms is colored faintly pinkish by the excess of permanganate. Salts of iron and chromium interfere.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 00165 = Mn$
" " " $\times \cdot 00213 = MnO$
" " " $\times \cdot 00261 = MnO_2$

ESTIMATION OF MANGANESE IN THE HIGHER OXIDES.

By Distillation with Hydrochloric Acid.

When the higher oxides of manganese are distilled with hydrochloric acid, chlorine is given off in an amount proportional to the excess of oxygen over that necessary to form protoxide.

$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + 2Cl$
$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + 2Cl$
$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$
$K_2MnO_4 + 8HCl = 2KCl + MnCl_2 + 4H_2O + 4Cl$
$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl$

The oxide to be estimated is placed in the flask *a*, Fig. 31, hydrochloric acid added, and the chlorine distilled into the U tube containing a solution of potassium iodide. The iodine is then estimated by adding starch and titrating with $\frac{n}{10}$ sodium thiosulphate.

c. c. $\frac{n}{10}$ thiosulphate × ·01145 = Mn_3O_4
" " " × ·0079 = Mn_2O_3
" " " × ·00435 = MnO_2
" " " × ·004931 = K_2MnO_4
" " " × ·003163 = $KMnO_4$

BY DIGESTING THE OXIDE WITH OXALIC AND SULPHURIC ACIDS.

When an oxide of manganese (with the exception of MnO) is digested with oxalic acid in presence of free sulphuric acid, the oxalic acid is converted into carbon dioxide and water, and manganese sulphate is formed.

$$Mn_3O_4 + C_2H_2O_4 + 3H_2SO_4 = 3MnSO_4 + 2CO_2 + 4H_2O$$

$$Mn_2O_3 + C_2H_2O_4 + 2H_2SO_4 = 2MnSO_4 + 2CO_2 + 3H_2O$$

$$MnO_2 + C_2H_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$$

$$K_2MnO_4 + 2C_2H_2O_4 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 4CO_2 + 4H_2O$$

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

The finely-powdered oxide is treated with an excess of oxalic acid, to which some dilute sulphuric acid has been added. After the oxide completely dissolves, the solution is diluted and titrated with permanganate.

c. c. normal oxalic acid × ·1145 = Mn_3O_4
" " " " × ·079 = Mn_2O_3
" " " " × ·0435 = MnO_2
" " " " × ·0493 = K_2MnO_4
" " " " × ·0316 = $KMnO_4$

BY DIGESTING THE OXIDE WITH SULPHURIC ACID AND AN EXCESS OF FERROUS SULPHATE.

$$Mn_3O_4 + 2FeSO_4 + 4H_2SO_4 = 3MnSO_4 + Fe_2(SO_4)_3 + 4H_2O$$

$$Mn_2O_3 + 2FeSO_4 + 3H_2SO_4 = 2MnSO_4 + Fe_2(SO_4)_3 + 3H_2O$$

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O$$

$$K_2MnO_4 + 4FeSO_4 + 4H_2SO_4 = K_2SO_4 + MnSO_4 + 2Fe_2(SO_4)_3 + 4H_2O$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

The ferrous salt may be either iron wire, dissolved in sulphuric acid, or ferrous ammonium sulphate.

Weigh the oxide of manganese, place in the flask Fig. 28, introduce the solution of ferrous sulphate with some dilute sulphuric acid, and pass a current of hydrogen or carbon dioxide through the apparatus.

The flask is heated until the oxide is dissolved, the lamp taken away, the flask allowed to cool while the current of hydrogen is still passing, the cork removed, and the solution diluted and titrated with $\frac{n}{10}$ permanganate for excess of ferrous salt.

c. c. $\frac{n}{10}$ ferr. amm. sulph. × ·01145 or met. iron × 2·0446 = Mn_3O_4
" " " " " × ·0079 " " × 1·4107 = Mn_2O_3
" " " " " × ·00435 " " × ·7767 = MnO_2
" " " " " × ·00493 " " × ·8869 = K_2MnO_4
" " " " " × ·00316 " " × ·5647 = $KMnO_4$

ESTIMATION OF MANGANESE IN SMALL QUANTITIES.

LECLERC* boils the substance with nitric acid and lead peroxide, and determines the permanganate formed by titration with a normal solution of mercurous nitrate in the cold. Chatard[*] boils the substance with nitric acid and lead peroxide, and titrates with a normal solution of ammonium oxalate.

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* Fres. Zeit. 12, 308.

Pichard[†] employs the same method for the estimation of small quantities of manganese in iron and steel. The amount of manganese is, however, found by color comparison with a solution containing a known amount of potassium permanganate. (See also Peters, Chem. News, xxxiii. 35.)

These methods are only useful where small amounts of manganese are present. With large quantities, the conversion into permanganic acid is not complete.

ESTIMATION OF MANGANESE IN ITS ORES, PYROLUSITE, BRAUNITE, ETC.

THE finely-powdered ore is first heated in an air-bath at 120° until it ceases to lose weight. The loss is moisture. As the powder absorbs moisture rapidly by exposure to the air, it should be kept in a tightly-stoppered vial. When a portion is required for analysis, the vial is weighed, about the required amount poured out, and the vial re-weighed. The difference between the two weighings is the amount taken. Some manganese ores contain magnetic oxide of iron, and this dissolved in acid produces a ferrous and a ferric salt; consequently neither the oxalic acid nor the ferrous ammonium sulphate method will, in this case, give correct results; as in addition to the permanganate required for the excess of oxalic acid or double iron salt, a portion is also used by the ferrous salt arising from the dissolved magnetic oxide.

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[*] Fres. Zeit. 11, 308.

[†] Comptes Rendus, 75, 1821.

Since the commercial value of manganese ore depends directly upon the amount of chlorine which it produces when heated with hydrochloric acid, it is always advisable to make the analysis by this method, which is described on page 112. If either of the other methods be used, the ore should first be tested with an astatic needle and the absence of magnetic oxide ascertained.

ESTIMATION OF THE AMOUNT OF ACID REQUIRED TO DECOMPOSE A MANGANESE ORE.

One gm. of the ore is heated in a flask with about 10 c. c. of hydrochloric acid (sp. gr. about 1·1) until the ore is dissolved. The flask containing the ore is connected with an inverted condenser, so that the acid which volatilizes flows back, and only the chlorine is expelled. The solution is filtered, diluted to a definite volume, and a portion taken out with a pipette and titrated with Kieffer's Solution, for the free acid remaining. The strength of the acid used for dissolving the ore is found in a similar manner, and the difference gives the amount used.

ESTIMATION OF MANGANESE IN SPIEGEL EISEN.

Spiegel eisen is an alloy of manganese and carbide of iron, and its value depends chiefly upon the amount of manganese it contains. This may be determined volumetrically as follows: 5 gms. of the alloy, in fine pieces, is dissolved in nitric acid in a small flask of hard glass, and evaporated to hard dryness, then heated until the bottom of the flask is dull red, and allowed to cool. The iron is now present as ferric oxide, and the manganese as Mn_2O_3. The amount of the latter cannot, according to Parry[*] and Galbraith,[†] be determined by the amount of chlorine which it evolves, but the mixed oxides, when treated with oxalic acid, evolve carbon dioxide in exact proportion to the Mn_2O_3 present, according to the equation $Mn_2O_3 + C_2H_2O_4 + 2H_2SO_4 = 2MnSO_4 + 2CO_2 + 3H_2O$. The oxides are treated in the flask with an excess of oxalic and hydrochloric acids, and the carbon dioxide given off collected in a tube over mercury. The carbon dioxide is then absorbed by a little caustic potassa solution, and from the loss in volume, proper correction for temperature, pressure, etc., being applied, the amount of manganese is calculated. Parry describes a special apparatus for the purpose, for a description of which, and further details, the original paper must be consulted.

Galbraith[‡] finds that the Mn_2O_3 in the mixed oxides may also be determined by treating them with ferrous ammonium sulphate and acid in excess, and estimating the excess of ferrous salt by $\frac{n}{10}$ permanganate. Hydrochloric acid is added to dissolve the oxides after the addition of the double iron salt; but this is objectionable where permanganate is the titrating fluid, and sulphuric acid should be employed instead, or bichromate used for titrating.

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[*] Chem. News, xxix. 86.

[†] American Chemist, vi. 462.

[‡] Amer. Chemist, vi. 462.

IRON.

IRON forms two series of salts, the ferrous and ferric, which by means of appropriate reagents can be converted one into the other. It is upon this property that the volumetric estimation of iron depends.

ESTIMATION OF FERROUS SALTS.

By Potassium Permanganate.—When an acid solution of a ferrous salt—ferrous sulphate, for example—is mixed with a solution of potassium permanganate, the following reaction takes place:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

When the ferrous is completely converted into ferric salt, a further addition of permanganate communicates its pinkish tint to the solution. The ferrous salt is strongly acidified with dilute *sulphuric* acid diluted (about a litre of fluid for 1. gm. iron) and permanganate run in from the burette, with constant shaking, until the solution takes permanently a very faint pinkish tint. As the permanganate is added, the solution takes gradually a faint brownish tint from formation of manganous and ferric sulphates, but this does not interfere with the sharpness of the reaction. If the solution becomes brown and turbid during the addition of permanganate, this shows that sufficient acid has not been added, and the whole process must be repeated.

ESTIMATION OF FERROUS SALTS IN HYDROCHLORIC ACID SOLUTION BY MEANS OF PERMANGANATE.

Löwenthal and Lenssen* have shown and Fresenius has confirmed their statement, that in presence of hydrochloric acid, ferrous salts are not acted upon by permanganate in strict accordance with the above equation; the following reaction also taking place:

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl$$

The chlorine so formed does not act upon the iron in dilute solution. Further than this, the amount of permanganate required varies with the concentration of the fluid amount of hydrochloric acid and temperature. The following process is recommended by Fresenius in presence of chlorine:

"Standardize the permanganate by means of iron dissolved in dilute sulphuric acid, make the iron solution to be tested up to ¼ litre, add 50 c. c. to a large quantity of water acidified with sulphuric acid, add permanganate from burette, then 50 c. c. of the iron solution, permanganate again, etc., etc. The numbers found the third and fourth time are taken. These are constant, while that obtained the first time, and sometimes also the second time, differ. The result multiplied by 5 gives exactly the quantity of permanganate proportional to the amount of protoxide of iron present."

Follenius† has tested the statement of Finkener (in Rose's Analytische Chemie) that hydrofluoric acid prevents the disturbing action of HCl, and find it to be entirely without foundation. It is by far the best plan, when solutions containing hydrochloric acid are to be titrated, to employ potassium bichromate as the oxidizing agent instead of permanganate, since it gives equally good results when carefully executed, and is not influenced by hydrochloric acid in dilute solution.

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* Fres. Zeitschrift, 1, 329.

† Ibid. 11, 177.

REDUCTION OF FERRIC SALTS TO THE FERROUS STATE PREVIOUS TO TITRATION WITH PERMANGANATE.

The best method of accomplishing this is by means of metallic zinc in acid (preferably sulphuric) solution. The zinc employed for this purpose must be free from iron. It is best to employ amalgamated zinc and small scraps of platinum, since this effects the reduction in a shorter time and with less consumption of zinc. The best form of vessel for effecting the reduction is shown in Fig. 35. A few pieces of granulated and amalgamated zinc are placed in the bottom, and then a coil of thin platinum foil is placed above this in such a way that the vessel may be inverted without allowing the zinc to fall out. The solution containing the ferric salt is poured into this glass, some dilute sulphuric acid added, the vessel covered with a watch-glass and allowed to stand until a small drop taken out with a glass rod and tested with potassium sulphocyanide gives no red coloration. The solution is then poured from the vessel into a beaker, the vessel washed with water, and the solution titrated with $\frac{n}{10}$ permanganate.

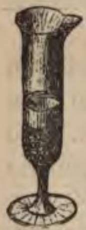

FIG. 35.

A still better apparatus for the reduction is a small platinum dish into which the iron solution is poured, a small piece of amalgamated zinc added, and the dish covered with a watch-glass. Reduction is very rapidly effected, owing to the large surface of platinum exposed. Sulphurous acid is sometimes used for the reduction, but the solution must be boiled for a considerable time before the excess is expelled, and it is not so good as zinc. In some cases it is best to precipitate the iron as sulphide by adding first ammonia, then ammonium sulphide, filtering and washing the precipitate out of contact with the air, and digesting it with an excess of an acid solution of ferric sulphate, just as zinc is determined in a similar way. In this case only one third of the permanganate used must be counted, since one equivalent ferrous sulphide produces three equivalents ferrous sulphate.

$$FeS + Fe_2(SO_4)_3 = 3FeSO_4 + S$$

c. c. $\frac{n}{10}$ permanganate × ·0056 = Fe
" " " × ·0072 = FeO
" " " × ·0080 = Fe_2O_3

TITRATION OF FERROUS SALTS BY MEANS OF POTASSIUM BICHROMATE.

When a ferrous salt is in contact with an acid solution of potassium chromate, the chromic acid is reduced, a salt of chromium formed, and the iron is converted into the ferric state. With bichromate, ferrous chloride and hydrochloric acid, for example, the reaction is as follows: $6FeCl_2 + K_2Cr_2O_7 + 14$

$HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O$. The chromium chloride has a greenish color, which it imparts to the solution. The end of the reaction is found by taking out a drop of the fluid, from time to time, and dropping it in a drop of fresh solution of potassium ferricyanide on a porcelain plate. As long as any ferrous salt remains, a blue color (Turnbul's Blue) results; but as soon as the ferrous salt is fully oxidized, a drop produces only a very faint dark-brown color with the ferricyanide. The method is an excellent one, and the proper stopping point shown very distinctly by the ferricyanide. The quantity of the solution used in testing is so small that it has no influence on the results.

The ferrous compound is dissolved in hydrochloric acid and $\frac{n}{10}$ bichromate run in, testing from time to time as above directed. The blue color of the test decreases in intensity as the ferrous salt is oxidized, so that we can judge from the color how much to add before repeating the test. The method is chiefly used when it is impossible to avoid the presence of chlorine in the solution to be titrated.

REDUCTION OF FERRIC SALTS PREVIOUS TO THE TITRATION WITH BICHROMATE.

The following method, in addition to those given on page 121 may be used.* The solution containing out ·5 gms. iron is diluted to 500 c. c. and heated boiling. Stannous chloride solution is then slowly, until a drop taken out gives only a k tint with a drop of potassium sulpho-

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[*] Chem. News, xxx. 221; Ibid. xxxi. 63.

cyanide. Three drops of standard bichromate are then added to the cold solution, and a drop again taken out and tested with potassium sulphocyanide. A distinct access of color in this test, as compared with the last test made in reducing, is accepted as proof of the absence of stannous salt, and it only remains to complete the titration in the usual manner. The reduction cannot be performed by means of zinc, since zinc ferricyanide is insoluble and obscures the end reaction.

ESTIMATION OF IRON IN FERRIC SALTS.

By Sodium Thiosulphate.—When a ferric salt is treated under proper conditions with a solution of sodium, thiosulphate, a ferrous salt, and tetrathionic acid are produced—$2Na_2S_2O_3 + Fe_2Cl_6 + 2HCl = H_2S_4O_6 + 4NaCl + 2FeCl_2$. The solution must be tolerably concentrated, and must contain a slight excess of hydrochloric acid, but not sufficient to cause a precipitate of sulphur upon addition of the thiosulphate.

A small quantity of a solution of pure copper sulphate (1 c. c. of a 1 % solution) is added to the ferric salt, and then a few drops of a solution of potassium sulphocyanide, which colors the fluid intensely red. Sodium thiosulphate is then run in slowly from the burette. A few minutes should elapse after each addition of thiosulphate. When the color communicated by the sulphocyanide has disappeared, a milkiness makes its appearance, due to cuprous sulphocyanide, which is formed. This marks the completion of the reaction. The operator is very apt to overstep the mark, and the best plan is to add thiosulphate in very slight excess, and find the amount in excess by adding starch, and titrating back with iodine. The method is tolerably good and sufficiently accurate for technical estimations, but not entirely satisfactory where great exactness is required. The copper sulphate is supposed by Oudemans,[*] who first used it, to act by transferring oxygen from the ferric salt to the thiosulphate. The estimation may be made without adding it, if the solution be heated to 40°.

$$\text{c. c. } \tfrac{n}{10} \text{ thiosulphate} \times \cdot 0056 = \text{Fe}$$

By Stannous Chloride.—The ferric salt, in somewhat concentrated hydrochloric acid solution, is heated, and the stannous chloride run in from a burette until the color has completely disappeared. The solution is then rapidly cooled by placing it in cold water, starch solution added, and the excess of stannous chloride found by $\frac{n}{10}$ iodine.

With care the results are sufficiently accurate for technical purposes, and the method is to be commended on account of the great number of analyses which may be executed in a short time.[†]

$$\text{c. c. } \tfrac{n}{10} \text{ stannous chloride} \times \cdot 0056 = \text{Fe}$$

By Digesting with Potassium Iodide.—When potassium iodide is added to a solution containing ferric chloride and an excess of hydrochloric acid, the following reaction occurs: $Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + 2I$.

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[*] Chem. News, xxii. 256.

[†] Ibid. xxxiv. 65.

The iodine remains in solution in the excess of potassium iodide, and may be measured by $\frac{n}{10}$ thiosulphate. All other substances capable of liberating iodine from potassium iodide, must of course be absent.

The digestion with potassium iodide is best performed in the bottle, Fig. 30, at a temperature of 60°. The solution is kept at this temperature 15 minutes to half an hour. Before closing the bottle, it is well to displace the air by carbon dioxide, which may be done by dropping in a crystal of sodium bicarbonate. After the decomposition is complete, the bottle is allowed to cool, starch added, and titrated with $\frac{n}{10}$ thiosulphate. The method gives excellent results.

$$\text{c. c. } \frac{n}{10} \text{ thiosulphate} \times \cdot 0056 = \text{Fe}$$

ESTIMATION OF FERROUS AND FERRIC SALTS IN A MIXTURE OF THE TWO.

Dissolve the compound in hydrochloric or sulphuric acid in a flask through which a current of hydrogen or carbon dioxide is passing, cool the solution, dilute it, and estimate the ferrous salt, if in hydrochloric acid solution, by means of bichromate: if in sulphuric acid solution, by means of permanganate. Dissolve a second portion of the substance, reduce to the ferrous state, and then add permanganate or bichromate until completely oxidized. The first estimation gives the amount of iron present in the ferrous state, and the second the total iron.

Subtracting the first from the second gives the iron present as ferric salt.

ESTIMATION OF SMALL QUANTITIES OF IRON.*

Small quantities of iron may be estimated with great exactness by color titration with potassium ferrocyanide.

We need solutions of

1. Ferric Chloride—made by dissolving 1·004 gms. iron wire in hydrochloric acid, oxidizing with nitric acid, and precipitating with ammonia. The precipitate is washed with hot water, dissolved in hydrochloric acid, and diluted to a litre. ·1 c. c. of this solution = ·001 gm. iron. If very small quantities are to be measured, the solution may be made $\frac{1}{10}$ the above strength, by diluting 100 c. c. to a litre.

2. Potassium Ferrocyanide. ·1 gm. salt to 20 c. c. water.

The solution in which the iron is to be estimated is made up to 100 c. c. in a glass cylinder or large test tube, and 1 c. c. nitric acid and 1 c. c. of the potassium ferrocyanide solution added.

In another cylinder of precisely the same shape, and made of the same glass, 100 c. c. of water are placed, and 1 c. c. nitric acid and 1 c. c. ferrocyanide added. The ferric chloride solution is then run into this second cylinder until the color corresponds to that of the first. For every volume of ferric chloride solution added to the second cylinder, we must add a like amount of water to the first, so that the volume of the two liquids shall remain the same.

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* Chem. News, xxx. 257.

After each addition of ferric chloride, the solution in the cylinder must be stirred by means of a bulb blown upon the end of a glass tube. The method is only accurate for the estimation of iron in very small quantities.

ESTIMATION OF IRON IN IRON ORES.

MAGNETIC IRON.

THE iron is here present, partly as ferrous and partly as ferric oxide. The proportions in which the two are present, usually approach closely $\cdot 1 \mathrm{eq} FeO = 37\cdot 03\ \%$ to $1 \mathrm{eq} Fe_2O_3 = 68\cdot 97\ \%$. The amount of FeO is found by dissolving the finely-powdered ore in hydrochloric acid in a flask through which hydrogen is passing, and titrating the solution with $\frac{n}{10}$ bichromate.

$$\text{c. c. } \frac{n}{10} \text{ bichromate} \times \cdot 0072 = FeO$$

The percentage of Fe_2O_3 is found by dissolving a second portion of the ore in sulphuric acid, reducing with zinc, and titrating with $\frac{n}{10}$ permanganate. This gives the total iron, from which the ferrous oxide found is subtracted. If the ore is not easily soluble in sulphuric acid, it is dissolved in hydrochloric acid, the iron reduced to the ferrous state by means of sulphurous acid, and the total iron estimated by means of bichromate. The ferric oxide may also be estimated by dissolving the ore in hydrochloric acid in an atmosphere of hydrogen, and determining the ferric oxide by heating the slightly acid solution with potassium iodide in excess in the stoppered bottle, Fig. 30, and the liberated iodine found by $\frac{n}{10}$ thiosulphate.

$$\text{c. c. } \tfrac{n}{10} \text{ solution} \times \cdot 0080 = Fe_2O_3$$

It frequently happens that magnetic iron ore, when dissolved in acid, leaves an insoluble residue containing iron. The amount of iron contained in this residue may be found by treating it in the manner of a silicate. (See below.)

ESTIMATION OF IRON IN SILICATES.

The estimation of the ferrous and ferric oxides in silicates is best made by a method devised by Cooke.* He uses the apparatus shown in Fig. 35*. The copper water-bath in the centre is provided with three tubes, one connected with a Mariotte flask to maintain the water at a constant level, a second to carry off the overflow, and a third which is connected with an apparatus for supplying a constant current of CO_2. The water-bath has a groove around the upper edge, in which an inverted funnel is placed and the spray and condensed steam make of this a water-joint which is perfectly tight.

The silicate in fine powder is mixed with hydrofluoric and sulphuric acids, and the platinum crucible containing it placed inside the funnel upon the water-bath. Water is then poured into the water-joint, the funnel filled with carbon dioxide, and the lamp lighted. As soon as the water boils, the current of CO_2 may be discontinued, and the decomposition allowed to proceed in the atmosphere of steam. The mixture may be stirred from time to time by introducing a platinum wire through the neck of the funnel, and fresh acid may be added through a funnel tube. When the decomposition is complete, the lamp is removed, and CO_2 again

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* Am. Jour. Sci. 2d ser., xliv. 347.

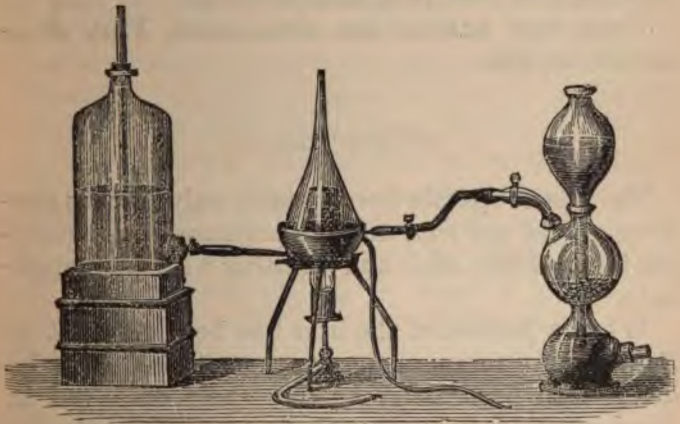

FIG. 35*.

run through the apparatus. The tube of the Mariotte flask is raised, until a current of water flows through the water-bath, and quickly cools it to the temperature of the air. The contents of the crucible are washed into a beaker, dissolved in water, diluted, and titrated with $\frac{n}{10}$ permanganate. The total iron in the solution may then be found by evaporating to a small bulk, reducing with zinc, and titrating with permanganate. Subtracting from this the iron present as FeO, we have remaining the iron in the state of Fe_2O_3.

The hydrofluoric acid of commerce generally contains sulphurous acid, due to its having been prepared in leaden vessels. Before being used, this must be converted into sulphuric acid, by adding a solution of permanganate until a faint pink tint remains.

Instead of hydrofluoric acid, finely powdered cryolite, free from iron, may be used.*

Upon this subject see also Leeds, Fres. Zeitschrift, 16, 323.

SPATHIC IRON.

The purest spathic iron contains only ferrous carbonate, and the iron may be estimated by dissolving in sulphuric acid and titrating with permanganate.

When a portion of the iron has been oxidized to Fe_2O_3 by the action of the weather, it may either be determined separately, or the whole dissolved in sulphuric acid, reduced with zinc, and titrated with permanganate.

CHROMIC IRON.

The great difficulty in the analysis of chromic iron is to dissolve it perfectly. In all cases it is necessary that the ore should be *very finely* powdered, so that it has no gritty feeling between the teeth.

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* Wilbur and Whittlesey, Chem. News, xxii. 2.

Genth's Process.—The following description of this method is taken from Fresenius:

"Take 0·5 gm. of the impalpable powder, and fuse in a capacious platinum crucible with 6 gm. bisulphate of potassa for fifteen minutes at a temperature scarcely above the fusing point of the latter, then raise the heat somewhat, so that the bottom of the crucible may just appear red, and keep it so for fifteen or twenty minutes. The fusing mass should not rise higher than half-way up the crucible. The mass begins to fuse quietly, and abundant fumes of sulphuric acid escape. At the expiration of twenty minutes the heat is increased as much as necessary to drive out the second equivalent of sulphuric acid, and even to decompose partially the sulphate of iron and chromium. To the fused mass now add 3 gm. pure carbonate of soda, heat to fusion, and add in small portions from time to time during an hour 3 gm. nitre, maintaining a gentle red heat all the while; then heat for fifteen minutes to bright redness. Treat the cold mass with boiling water, filter hot, wash the residue with hot water, then digest in the heat with hydrochloric acid. If any thing remains undissolved, it is a portion of the ore undecomposed, and must be subjected again to the above operation. To weigh such a residue and deduct it from the ore first taken is not good, as it never possesses the composition of the original substance." Evaporate the solution to dryness with an excess of sulphuric acid to drive off most of the hydrochloric acid, dissolve, reduce with zinc, and titrate with permanganate. "The alkaline solution, which often contains, besides the chromic acid, also some silicic, titanic, and manganic acids, and alumina, is evaporated with excess of nitrate of ammonia on a water-bath nearly to dryness and till all the free ammonia is expelled. On addition of water, the silicic acid, alumina, titanic acid, and sesquioxide of manganese remain undissolved, while the chromic acid passes into solution, and is determined" by precipitating with $\frac{n}{10}$ lead solution. (See Chromium).

Britton's Process Modified.—0·5 gms. of the finely powdered ore is mixed in a platinum crucible with 4 gms. of a mixture of 1 part potassium chlorate and 3 parts soda lime. The crucible and contents is ignited at a bright red heat for an hour and a half, and allowed to cool. The mixture does not fuse but sinters to a coherent mass, and may be shaken from the crucible into a beaker, leaving the inside of the crucible clean and bright. The mass is digested with hot water, and hydrochloric acid added until all dissolves with the exception of a few flakes of silica. Add solution of sodium hydrate, free from organic matter, until all the iron and a portion of the calcium are precipitated as hydrates; wash the precipitate, dissolve it in sulphuric acid, reduce with zinc, and determine the iron with permanganate. Acidify the filtrate with hydrochloric acid, add an excess of ferrous ammonium sulphate in known amount, and determine the excess by $\frac{n}{10}$ bichromate.

Dittmar's Method.—Five gms. of finely-powdered ore is fused with 5–6 gms. of a flux composed of two parts of borax fused with three parts of alkaline carbonates. The mixture of ore and flux is fused for five minutes in a covered crucible. The lid is then removed and the mass heated very strongly with constant stirring until the ore has all dissolved, and the fusion is then further continued for about three quarters of an hour. Oxygen is absorbed, and the chromium salt converted into a chromate. The fused mass is digested with water, heated over a water-bath, with the addition of a few drops of alcohol, so as to reduce any manganate if present; the liquid is filtered, and the residue washed with hot water. The solution is then added to an excess of a solution of ferrous ammonium sulphate or iron wire in dilute sulphuric acid, and the excess of iron found by titrating with $\frac{n}{10}$ bichromate.

ESTIMATION OF THE IRON IN CAST IRON AND STEEL (MOHR).

The amount of iron in cast iron and steel is usually determined by loss—the total percentage of impurities being taken from 100. By the following method, which has some resemblance to Gay-Lussac's silver assay, the amount of iron may be found directly with great accuracy. The amount of impurity in an iron seldom exceeds 5 per cent, and if we weigh out 1·05 gms. of the metal, we are sure to have at least 1. gm. iron.

1·05 gms. of the iron or steel is dissolved in hydrochloric or sulphuric acid, in an atmosphere of hydrogen, and 100 c. c. of potassium bichromate solution added. The potassium bichromate solution used is empirical, containing 8·785 gms. pure salt in the litre, and 1 c. c. being equal to 0·01 gm. iron.

The amount so added suffices to oxidize 1 gm. of the iron which was dissolved. The remainder is estimated with a decimal solution of potassium bichromate containing ·8785 gm. per litre, added from a burette, until a drop of the solution tested with potassium ferricyanide shows no blue color.

Instead of the above bichromate solution we may use the ordinary decinormal solution, taking about ·58 gms. of the impure metal for the analysis.

To obtain the greatest accuracy by this method, attention must be paid to the precautions mentioned under the head of Silver Alloys and Coin, so far as they relate to the manner of securing the greatest uniformity in the amount of fluid delivered by the 100 c. c. pipette. The strength of the bichromate must of course be very carefully determined.

NICKEL.

ESTIMATION AS OXALATE.*

THE nickel should be present as neutral sulphate. Add oxalic acid in excess and concentrate the solution on a water-bath. Then add an equal volume of alcohol, and digest for about half an hour, replacing the alcohol as fast as it evaporates. Collect the precipitate on a paper-filter, wash with alcohol, dry, and dissolve in dilute sulphuric acid. Cobaltous sulphate is then added until the solution becomes colorless, and then titrated with permanganate.

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* Amer. Jour. Sci. xiv. 204; Chem. News, xxii. 210.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 00294 = \text{Ni}$$

Other metals precipitable by oxalic acid must of course be absent.

On the estimation of nickel see also Wicke, Fres. Zeit. 4, 424.

COBALT.

COBALT SULPHATE.

OTHER sulphates must be absent. To convert cobalt compounds into the sulphate, they are first converted into the sesquioxide by treatment with potassium hydrate and hypochlorite, the precipitate of Co_2O_3 which is formed is washed, dissolved in sulphuric acid and heated to low redness till all excess of sulphuric acid is driven off. The sulphuric acid is then determined in this by $\frac{n}{10}$ barium chloride. (See Sulphuric Acid.)

$$\text{c. c. } \tfrac{n}{10} \text{ barium chloride} \times \cdot 00294 = \text{Co}$$

COBALT OXALATE.*

The solution must be neutral and free from other heavy metals. Oxalic acid is added, and an equal volume of alcohol, then allowed to stand, filtered through an asbestos filter, and the precipitate washed with alcohol and dried. It is then dissolved in sulphuric acid, nickelous sulphate added until a faint smoky blue takes the place of the pinkish color, and then titrated with permanganate.

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* Amer. Jour. Sci. xiv. 204; Chem. News, xxii. 210.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 00294 = \text{Co}$$

BY PERMANGANATE.*

Moist mercuric oxide obtained by precipitation is added to the neutral or slightly acid solution, and then permanganate until the fluid above the precipitate which forms is of a faint pinkish tint. Towards the end of the reaction the precipitate consists of Co_2O_3 and MnO_2, and settles rapidly. The strength of the permanganate must be found by titrating against a weighed amount of pure cobalt salt.

Manganese, organic matter, nitric acid, chlorine, or other oxidizing agents, must not be present. Small quantities of nickel have no effect.

CHROMIUM.

CHROMIUM is always estimated after previous conversion into chromic acid. This is easily effected by fusing the substance with potassium carbonate and chlorate.

ESTIMATION BY THE AMOUNT OF IODINE LIBERATED FROM KI.

By Digestion.—Pour the solution of the chromate acidified by HCl in the bottle, Fig. 30, and add a strong solution of potassium iodide, and, after stoppering tightly, heat gently for ten or fifteen minutes. Cool, take out the stopper, add starch, and titrate with $\frac{n}{10}$ thiosulphate.

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* Fres. Zeitschrift, 3, 266.

By the amount of Chlorine evolved.—The chromate may likewise be distilled with hydrochloric acid, the chlorine evolved received in a solution of potassium iodide, and the liberated iodine determined by $\frac{n}{10}$ thiosulphate. With potassium bichromate, the reaction is as follows:

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 6Cl$$

c. c. $\frac{n}{10}$ thiosulphate × $\cdot 001749 = Cr$
" " " × $\cdot 002549 = Cr_2O_3$
" " " × $\cdot 003349 = CrO_3$

Estimation by adding an excess of Ferrous Salt, and determining the excess.—The solution of ferrous ammonium sulphate may be used for this purpose, or a weighed quantity of the double salt or of iron wire may be dissolved and added to the chromate. If the iron salt is in excess, a drop dipped out with a rod will strike the blue color with potassium ferricyanide. The excess of ferrous salt is then estimated by bichromate. (See Iron.)

By precipitation as Lead Chromate.—The solution must not contain a large excess of free acid. A quantity of sodium acetate is added, more than sufficient to saturate the mineral acid and set free an equivalent of acetic acid. Lead acetate is then added, the solution filtered through a funnel with a plug of asbestos in the neck, and the lead chromate washed. The asbestos containing the chromate is then transferred to a flask, the funnel washed into the flask, hydrochloric acid and ferrous salt in excess added, and the excess of ferrous sulphate added determined by bichromate. The lead chromate is decomposed by the ferrous salt somewhat slowly, and it is best to heat the flask and conduct a stream of CO_2 or H through it during the digestion.

The precipitated lead chromate may also be digested with KI in the stoppered bottle, Fig. 30, and the iodine measured by $\frac{n}{10}$ thiosulphate.

$$\text{c. c. } \tfrac{n}{10} \text{ thiosulphate} \times \cdot 003349 = CrO_3$$

By precipitation as Lead Chromate with Standard Lead Solution.—This precipitation is the reverse of that used in the estimation of lead, and the solutions employed are the same. The chromic acid should be in acetic acid solution, and should contain an excess of sodium acetate.

ALUMINUM.

Aluminum can only be estimated volumetrically when it occurs as potassium or ammonium alum. The alum must not contain an excess of acid.

Barium chloride is added until the sulphuric acid is completely precipitated, and then, without filtering, litmus added, and normal ammonium or sodium hydrate run in until the color changes to blue.

c. c. normal alkali × $\cdot 01708 = Al_2O_3$
" " " × $\cdot 15813 =$ Cryst K alum.

URANIUM

MAY be estimated, like iron, by reduction with zinc to the uranous state, and then oxidizing with permanganate;* or

By precipitation with the standard solution of phosphoric acid; the process being the reverse of that used for the estimation of phosphoric acid.

TIN.

TIN is estimated in the form of stannous chloride. It may easily be brought into this condition by precipitating the metal from the solution containing it by means of pure metallic zinc, washing the finely divided tin, and dissolving in strong hydrochloric acid in contact with pieces of metallic platinum in an atmosphere of hydrogen, or carbon dioxide. A solution of double potassium and sodium tartrate (Rochelle salt) is added, and then a strong solution of sodium bicarbonate, until the solution is alkaline. If the solution becomes cloudy upon addition of the sodium bicarbonate, more Rochelle salt must be added. Starch solution is then added, and $\frac{n}{10}$ iodine solution from a burette until the blue color appears.*

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* See Belohoubek, Fres. Zeit. 6, 120; 16, 104; Follenius, Fres. Zeit. 11, 179, finds that HCl has the same influence as with iron salts, and when it is unavoidably present, the same process may be used; namely, titrating a portion of the solution, adding a second portion, titrating again, etc.

$$\text{c. c. } \frac{n}{10} \text{ iodine} \times \cdot 0059 = \text{Sn}$$

TITANIUM.

Titanium is most frequently met with as titanic oxide TiO_2, and may be estimated as follows:

Fuse the finely-powdered oxide with 8–10 times its weight of potassium or sodium bisulphate, and allow to cool completely. Place the fused mass together with the crucible, in 200–300 c. c. of water, add some dilute H_2SO_4 and allow it to stand until it dissolves. Some pieces of amalgamated zinc and platinum scraps are then placed in the solution, and reduction allowed to proceed in the cold. The titanic oxide is, after a considerable lapse of time—twelve to eighteen hours—converted into titanous oxide Ti_2O_3. After the reduction is complete, the solution is poured into a beaker, and titrated with permanganate.†

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* Upon the estimation of tin see also Mohr, Vierte Auflage, 235, 264, 266, 311; Goppelsröder und Trechsel, Fres. Zeit. 16, 364.

† If the substance be titaniferous iron ore, or if the titanic oxide contains iron, this too will be reduced by the zinc and oxidized by permanganate. In such cases, a part of the solution is reduced with sulphurous acid and titrated, then an equal portion by means of zinc. In the first case, the iron alone, in the second, both iron and TiO_2 are reduced, and by subtraction the permanganate equivalent to the TiO_2 present is found.

$$MnO_4 + 5Ti_2O_3 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10TiO_2 + 3H_2O$$

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 0050 = Ti$$
$$\text{`` `` ``} \times \cdot 0082 = TiO_2$$

MOLYBDENUM AND TUNGSTEN.

MOLYBDENUM usually occurs as molybdic acid,
O_3 or as a molybdate. This is dissolved in dilute
phuric acid, reduced with amalgamated zinc, like
n, and titrated with permanganate. The supposi-
n has been that the MoO_3 is reduced to Mo_2O_3 by
zinc.* According to Werncke,† however, the re-
tion is not complete; but if the results be calcu-
ed upon the supposition that an oxide having the
nposition $Mo_{12}O_{19}$ is formed, nearly correct re-
ts are obtained. It is impossible to specify any
e for the complete reduction, as this depends
n the dilution, temperature, etc. The results
en by Werncke show that the method is scarcely
stworthy. The same may be said of a similar
cess for Tungsten.

ARSENIC.

ESTIMATION OF ARSENIOUS OXIDE BY IODINE.

WHEN arsenious oxide in alkaline solution is
ated with iodine, it is oxidized to arsenic oxide.

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* Fres. Zeitschrift, 4, 420; 5, 203.

† Ibid. 14, 1.

$$As_2O_3 + 2H_2O + 4I = As_2O_5 + 4HI$$

If the solution is acid, it is neutralized by means of sodium carbonate, and then 20–25 c. c. of a saturated solution of sodium bicarbonate added for every 1 gm. As_2O_3 in solution. Starch is then added and $\frac{n}{10}$ iodine run in from a burette, until the blue color remains permanent.

$$\text{c. c. } \frac{n}{10} \text{ iodine} \times \cdot 00495 = As_2O_3$$

By distillation with chromic acid.* When potassium bichromate is boiled with hydrochloric acid, chlorine is given off in accordance with the following reaction:

$$K_2Cr_2O_7 + 14HCl = 2KCl_2Cr + 7H_2O + 6Cl$$

One molecule CrO_3 giving 3 atoms chlorine. If arsenious oxide be present, it is oxidized to arsenic oxide at the expense of a part of the chlorine, and less is therefore given off. $As_2O_3 + 4Cl + 2H_2O = As_2O_5 + 4HCl$. The excess of chlorine evolved from a measured quantity of bichromate over that required to oxidize the arsenious to arsenic oxide is received in a solution of potassium iodide, and the iodine titrated with $\frac{n}{10}$ thiosulphate. If we let a represent the c. c. of $\frac{n}{10}$ bichromate taken, and b the c. c. of $\frac{n}{10}$ thiosulphate used,

$$a - b \times \cdot 001958 = As$$
$$a - b \times \cdot 00495 = As_2O_3$$

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* Annal. d. Chem. u. Pharm. 86, 290.

ARSENIOUS SULPHIDE.

Freshly precipitated arsenious sulphide may be dissolved in ammonium carbonate and some precipitated bismuth subnitrate added, and the solution boiled. By this process the sulphur is completely removed, and arsenious oxide remains in solution. The liquid is filtered from the bismuth sulphide produced and the arsenious oxide in the filtrate measured with $\frac{n}{10}$ iodine. (Mohr.)

ESTIMATION OF ARSENIC OXIDE.*

Arsenic acid forms, with uranium nitrate or acetate, a salt analogous in composition to uranium phosphate, having the formula $2Ur_2O_3, As_2O_5$. This salt, like the phosphate, is insoluble in water and acetic acid. The estimation is made in precisely the same way as for phosphoric acid. As in the estimation of phosphoric acid, a correction must be applied for the bulk of liquid and amount of sodium acetate and acetic acid used. The end of the reaction is found by taking out a drop of the liquid and placing in a drop of potassium ferrocyanide, when, if an excess of uranium be present, a reddish brown line is formed at the junction of the two fluids.

Arsenic acid, like phosphoric, may be precipitated by magnesium mixture, and the precipitate, after being washed with alcohol, suspended in water and estimated with normal acid.† (See Magnesium, and Phosphoric Acid.)

$$\text{c. c. normal acid} \times \cdot 0575 = As_2O_5$$

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* Annal. d. Chem. u. Pharm. 117, 195.

† Stolba, Fres. Zeit. 16, 100.

ESTIMATION OF ARSENIC IN SMALL QUANTITIES.*

This method may be used according to Houzeau, for the estimation of arsenic and antimony in cases of poisoning. The substance containing them is placed in a Marsh's apparatus, and the gas given off passed into a measured amount of a solution of silver nitrate. A part of the silver is converted into arsenide or antimonide, and after filtration the remainder may be estimated by $\frac{n}{10}$ sodium chloride. (See Silver.)

ANTIMONY.

As Antimonious Potassium Tartrate.—When iodine is added to a solution of tartar emetic, the following reaction is supposed to take place:

$$\begin{gathered}2C_4H_4K(SbO)O_6 + 3H_2O + 4I = 2C_4H_5KO_6 + Sb_2O_5 \\ 4HI\end{gathered}$$

The reaction only takes place with regularity, however, in an alkaline solution; if the solution be acid, the amount of free acid as well as the dilution influences the result. Antimonious compounds may be converted into tartar emetic by digesting with tartaric acid and then adding sodium bicarbonate to alkaline reaction. Antimonious sulphide is dissolved in hydrochloric acid by the aid of heat, tartaric acid added, and then sodium bicarbonate to alkaline reaction, as above.

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* Comp. Rend. lxxv. 1823; Chem. News, xxvii. 74.

After bringing the antimony into alkaline solution, add starch solution, and then $\frac{n}{10}$ iodine, until the blue color is persistent for a few minutes.

$$\text{c. c. } \frac{n}{10} \text{ iodine} \times \cdot 0061 = \text{Sb}$$

BISMUTH.

By Precipitation as Chromate (*Mohr*). — The metal must be present as nitrate and must be free from chlorine. If not already in solution, it is dissolved in nitric acid, then ammonia added until a slight precipitate forms, and then dilute nitric acid until this is dissolved. Potassium bichromate is added in excess, and the solution heated until the precipitate subsides. The clear fluid is then tested with ammonia and potassium bichromate, and if neither of these produce a precipitate, the entire solution is poured upon an asbestos filter and washed with hot water. The precipitate and filter are then transferred to a flask, a weighed amount of ferrous ammonium sulphate and some sulphuric acid added, and the flask gently heated, while a stream of carbon dioxide or hydrogen is passing through it. The excess of ferrous salt is then found by titration with permanganate.

$$\text{Fe} \times 1 \cdot 238 = \text{Bi}$$

*By Precipitation with Standard Bichromate.**—The metal must be in nitric acid solution and contain no chlorine, nor other metals. Sodium acetate is added to the solution, until a copious white precipitate is thrown down. Acetic acid is then added in quantity sufficient to dissolve the precipitate completely and to insure that when the liquid is made up to a fixed volume, say to 250 c. c., no precipitate shall be formed. A certain volume of this liquid is withdrawn by means of a pipette, placed in a beaker and heated to boiling. The potassium bichromate is then gradually run in from a burette, the liquid being boiled between each addition of the solution, until a drop of the supernatant liquid gives a faint reddish brown coloration when spotted with silver nitrate on a white slab. The strength of the potassium bichromate is best found by titrating in a similar way against a known amount of bismuth. A convenient strength of bichromate is 10 gms. per litre.

By Iodic Acid.†

The bismuth must exist as nitrate; sodium bicarbonate is added until a precipitate is formed, and this is dissolved by adding acetic acid. The fluid is then heated to boiling and filtered if necessary; 25 c. c. of a solution of iodic acid (made by dissolving 30 gms. crystallized acid in a litre) are then added and the solution made up to 250 c. c. After it has stood some time, it is filtered through a dry filter,

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* Jour. Chem. Soc. vol. 1, 1876, p. 483; Ibid. vol. 2, 1877, p. 658.

† Monit. Scientifique, 3d ser. iii. 900.

100 c. c. taken out by means of a pipette, potassium iodide and dilute sulphuric acid added, and the iodine set free estimated by starch and sodium thiosulphate.

A portion of a solution of bismuth of known strength is then titrated as above directed, and from the data obtained the precipitating power of the iodic acid solution found.

LEAD.

ESTIMATION OF LEAD OXIDE AND CARBONATE.

MAY be estimated by dissolving them in a measured quantity of normal nitric acid and estimating the excess of acid by means of normal sodium carbonate. As soon as the free acid is completely saturated, further addition of sodium carbonate turns the fluid milky from separation of lead carbonate. Or,

Dissolve in an excess of normal nitric acid, add sufficient neutral potassium sulphate to precipitate all the lead, and then, without filtering, add litmus, and estimate the excess of nitric acid by normal alkali.

c. c. normal nitric acid $\times \cdot 10346 = Pb$
" " " " $\times \cdot 11146 = PbO$

Soluble salts of lead may be converted into carbonate and then estimated as above by adding a slight excess of ammonium carbonate to the watery solution and washing the precipitated carbonate with hot water.

BY DIGESTION OF THE CHROMATE WITH A FERROUS SALT.*

If the lead salt be acid, sodium acetate is added in sufficient quantity to saturate the mineral acid and set free an equivalent of acetic acid. Potassium bichromate is added to the warm solution, and the precipitated chromate collected on an asbestos filter and washed thoroughly with warm water. The precipitate, together with the asbestos, is placed in a flask containing a weighed quantity of ferrous ammonium sulphate, or iron wire dissolved in dilute sulphuric acid, and the solution heated, while a current of hydrogen or carbon dioxide is passing through the flask, until the chromate is completely decomposed. Lead sulphate is formed which is white, and the solution takes a greenish tint from the chromium sulphate which is formed. The excess of ferrous salt is estimated by $\frac{n}{10}$ permanganate or bichromate. $Fe \times 1{\cdot}2315 = Pb$.

ESTIMATION BY STANDARD POTASSIUM BICHROMATE.

The solution of bichromate used for the precipitation is the same as that used for the estimation of barium containing 7·3808 gms. of the pure salt per litre.

A second solution containing an equivalent quantity of lead is convenient where, as sometimes happens, the proper point is overstepped in adding the bichromate. This solution may be made by dissolving 16·546 gms. pure lead nitrate in water and diluting to a litre.

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* See also Hinman, Silliman's Jour. 1877, p. 478.

The lead solution must not contain much free acid. Sufficient sodium acetate is added to saturate the mineral acid and set free an equivalent of acetic acid. The above solution of bichromate is then added from a burette until all the lead is precipitated. This point is found by taking out a portion of the liquid from time to time by means of the filtering pipette and testing the clear liquid with a drop of bichromate. If the proper point is overstepped, a few c. c. of the lead solution are added and then the analysis completed as before. The lead chromate is very insoluble in water and acetic acid and the end of the reaction is very sharply defined. Moderate quantities of sulphuric and hydrochloric acids do not interfere, since sodium acetate dissolves lead chloride and sulphate.

Schwarz[*] uses a neutral solution of silver nitrate to find the ending of the reaction. As soon as an excess of the bichromate has been added, a drop of the solution tested on a porcelain plate with a drop of the silver nitrate shows the red color of silver chromate. Silver chromate is not entirely insoluble in free acetic acid, however, and if chlorine is present, this indicator cannot be used.

$$\text{c. c. } \tfrac{n}{10} \text{ bichromate} \times \cdot 010346 = \text{Pb}$$
$$\text{" \quad " \quad \quad "} \quad \times \cdot 011146 = \text{PbO}$$

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[*] Fres. Zeitschrift, 2, 378.

COPPER.

ESTIMATION WITH POTASSIUM IODIDE AND SODIUM THIOSULPHATE.*

WHEN a solution of cupric sulphate is added to potassium iodide, the following reaction occurs:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + 2I.$$

The cuprous iodide precipitates, and the iodine is titrated by $\frac{n}{10}$ thiosulphate. The solution of copper should be in the form of sulphate—nitric and hydrochloric acid must not be present. The solution should be so strong that 100 c. c. contain at least 1. gm. copper. Copper may be changed into the form of sulphate by precipitating as sulphide in hot acid solution by H_2S dissolving in nitric acid, and evaporating the solution to dryness after adding some sulphuric acid and sodium sulphate.

c. c. $\frac{n}{10}$ thiosulphate × ·006317 = Cu
" " " × ·007917 = CuO

BY PRECIPITATION AS CUPROUS OXIDE.

To the solution of copper, tartaric acid is added, and then sodium hydrate until the solution is of a clear blue color, grape or starch sugar is then added, [illegible] the solution heated to 90°, until all the copper [illegible] recipitated as Cu_2O, and an excess of grape [illegible] remains in solution. The solution must not be heated above 90°. The precipitated oxide must then be filtered through a funnel containing a plug of asbestos in the neck, washed out carefully with hot water, and the asbestos and cuprous oxide together transferred to a flask containing an acid solution of ferric sulphate. The solution is heated until the cuprous oxide is completely dissolved, and the resulting ferrous sulphate titrated with permanganate. While the cuprous oxide is dissolving, a stream of carbon dioxide or hydrogen should be led through the flask to prevent oxidation of the ferrous salt which is formed; the reaction is as follows:

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* Annal. d. Chem. u. Pharm. 91, 237.

$$Cu_2O + Fe_2(SO_4)_3 + H_2SO_4 = 2CuSO_4 + 2FeSO_4 + H_2O$$

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot006317 = Cu$$
$$\text{" " " } \times \cdot007917 = CuO$$

BY PRECIPITATION AS METALLIC COPPER.

The copper is precipitated from its solution, which must contain no nitric acid nor any other metal precipitable by zinc, by placing a piece of pure metallic zinc in the solution. As soon as precipitation is complete, the strip of zinc is removed, and any copper which adheres to it carefully washed off. The spongy mass of metallic copper is then washed either by decantation or upon the asbestos filter placed in a flask containing an acid solution of ferric sulphate, through which a stream of hydrogen is passed, and heated until the copper has completely dissolved.

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$$

c. c. $\frac{n}{10}$ permanganate × ·003158 = Cu
" " " × ·003958 = CuO

BY MEANS OF POTASSIUM CYANIDE.

When potassium cyanide is added to the blue ammoniacal solution of a copper salt, the solution loses its blue color, and copper and ammonium cyanide is formed. Cyanogen is also liberated, which reacts on the free ammonia, producing urea, urea oxalate, ammonium cyanide, and formate (Liebig). The reaction varies with the amount of free ammonia, ammoniacal salts, the concentration of the solution, and the temperature. The process, therefore, is worthless, unless all analyses made by it can be done under the same conditions. Manganese, nickel, cobalt, mercury, silver, and large quantities of zinc must first be removed. The value of the potassium cyanide solution changes from day to day, and must be determined afresh before every series of analysis by means of a standard solution of copper sulphate containing 39·356 gms. $CuSO_4 + 5H_2O$ per litre. 1 c. c. = ·01Cu.

BY SODIUM SULPHIDE.

Ammoniacal Solution.—The ammoniacal solu-
[illegible] st be heated to 60° to 80°—between these
[illegible] es an oxysulphide is precipitated, 5CuS,
[illegible] t the ordinary temperature CuS falls,
[illegible] subside so readily as the oxysul-

phide. If the precipitation is conducted at a higher temperature, another oxysulphide containing more oxygen is precipitated, and copper may remain in solution without coloring the fluid. The solution is placed over the lamp in a flask, and a thermometer inserted in the liquid; when the temperature reaches 75° the lamp is withdrawn and sodium sulphide added from a burette, shaking and allowing the fluid to clear, after each addition, until the blue color has completely disappeared. Or—as suggested by Mohr—until a drop of the solution taken out with a glass rod and placed upon filter-paper gives the black ring with the alkaline lead solution. In the latter case, the precipitation is made at ordinary temperatures, as in the case of zinc; and the same correction must be made here as there, for the excess of sodium sulphide necessary to show the reaction with the alkaline lead solution.

In Acid Solution.—The solution is diluted with hot water to about 200 c. c. in a stoppered flask (500 c. c.) acidified with HCl, and the sodium sulphide run in, replacing the stopper and shaking after each addition. The copper sulphide produced separates rapidly and leaves a clear solution above it. The sodium sulphide is added until no further precipitate is produced. The sodium sulphide decomposes slowly, and its strength is determined by means of a solution of copper sulphate containing 39·356 gms. $CuSO_4 + 5H_2O$ per litre. The determination of the strength of the sodium sulphide must of course be made as it is to be used; if the copper is to be determined in acid solution, the copper sulphate taken for the determination must be acidified. If, on the contrary, the estimation is to be made in an ammoniacal solution, the copper sulphate taken is made strongly ammoniacal.

ESTIMATION OF COPPER IN SMALL QUANTITIES.*

The solutions required are as follows:

Solution of copper sulphate. Made by dissolving ·3935 gms. $CuSO_4 + 5H_2O$ in a litre of water ·1 c. c. = ·0001 gm. Cu.

Solution of ammonium nitrate. 100 gms. of the salt in a litre.

Solution of potassium ferrocyanide. 1 part salt to 25 parts water.

The solution containing the copper whose amount is to be determined is placed in one of two cylinders holding rather more than 150 c. c. (the point corresponding to that volume being marked on the glass) and diluted to 150 c. c.; 5 drops ferrocyanide and 5 c. c. of ammonium nitrate are then run into both cylinders, the second cylinder then filled to the 150 c. c. mark with distilled water, and the standard copper solution run in from a burette until the tint is of the same depth as that of the solution in the first cylinder. The purple brown ferrocyanide is produced in very dilute solution, showing 1 part copper in 2,500,000 parts water. The ammonium nitrate is d to increase the delicacy of the reaction, which enhanced by other neutral salts, as potassium nd ammonium chloride. The results are te with small quantities of copper.

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* Chem. News, xxxii. 308.

Organic matter, such as sugar, etc., and lead, in not too large amount, do not influence the color.

ESTIMATION OF COPPER IN COPPER ORES (MOHR).

The ore is finely pulverized and 5 gm. weighed into a porcelain crucible, (100 m. m. diam.) covered with a watch-glass, strong nitric and a little sulphuric acid added, and the whole evaporated to dryness and heated until any unoxidized sulphur is burned off. After the crucible has cooled, add warm water and a little sulphuric acid, heat to boiling, and pour the clear fluid on a filter: leaving all the undissolved portion in the crucible. To this undissolved portion add nitric and sulphuric acid again, and evaporate to dryness as before. If the ore was finely pulverized, two evaporations suffice. The residue is treated with water and sulphuric acid as before, heated to boiling, and filtered through the same filter. We can now proceed in two ways:

1. The copper is precipitated as sulphide in hot solution, the copper sulphide collected on a filter, and washed. A hole is then punched through the filter, the sulphide washed into a porcelain crucible, and evaporated to dryness with nitric acid, a little sulphuric acid, and a few crystals of sodium sulphate. The residue is dissolved in water in the crucible, and the copper estimated with potassium iodide and thiosulphate by the method given page 150.

2. To the solution containing the copper a piece of pure metallic zinc is added, and the solution allowed to stand over night. The copper is completely

precipitated in the metallic state. The remaining piece of zinc is carefully cleaned from particles, the copper washed either by decantation or upon an asbestos filter, and the copper estimated by dissolving in ferric sulphate and determining the ferrous salt produced. (See page 151.)

Gold, silver, platinum, tin, lead, iron, zinc, nickel, cobalt, bismuth, arsenic, mercury, molybdenum, and antimony do not interfere with the accuracy of the process.

STEINBECK'S PROCESS.

5 gms. of finely-powdered ore are put into a flask with 40 to 50 c. c. crude hydrochloric acid (sp. gr. 1·16) and 6 c. c. nitric acid (prepared by mixing nitric acid sp. gr. 1·12 with its own bulk of water). s containing much sulphur or bitumen must be ted before being treated with acid. The flask is d on a sand-bath for half an hour, and then l for 15 minutes; then filtered into a large beak-l the residue washed with water. A rod of eighing about 50 gms. and as free from lead ible, is surrounded with a stout piece of m foil and immersed in the copper solution. ecipitation is usually complete in about half r. The precipitate of metallic copper is col-together with the platinum foil upon which has deposited, and if it amounts to 6% of the own approximately from its bulk), dissolved . of the nitric acid before mentioned. If %, it is dissolved in 16 c. c. nitric acid, c. c. and $\frac{1}{2}$ taken. To the solution of

copper 10 c. c. ammonia solution (prepared by mixing one volume sp. gr. 0·93 with two volumes water) is added, and the fluid titrated with potassium cyanide until the blue color has disappeared. (Compare page 152.)

MERCURY.

ESTIMATION OF MERCURY IN MERCUROUS SALTS BY PRECIPITATION AS CHLORIDE.

To the solution, which must contain all the mercury as mercurous salt, $\frac{n}{10}$ sodium chloride in excess is added. The precipitate is washed with water, and to the filtrate a few drops of potassium chromate added. If the solution is acid, the color is immediately changed to red, and sodium carbonate must be added until the fluid reacts neutral, or faintly alkaline, to test-paper. The excess of $\frac{n}{10}$ sodium chloride is then measured by titration with $\frac{n}{10}$ silver nitrate. (See Chlorine.)

c. c. $\frac{n}{10}$ sodium chloride $\times \cdot 0200 = Hg$
" " " " $\times \cdot 0208 = Hg_2O$

ESTIMATION OF MERCUROUS CHLORIDE (HEMPEL).

Potassium iodide and $\frac{n}{10}$ iodine are added to the mercurous chloride, until it is completely dissolved. Starch is then added, and the blue color taken away by $\frac{n}{10}$ thiosulphate and lastly $\frac{n}{10}$ iodine is again added until the blue color once more appears. Subtract the c. c. of thiosulphate from the total iodine, and the remaining c. c. will be a measure of the mercury.

$$\text{c. c. } \tfrac{n}{10} \text{ iodine} \times \cdot 0200 \ \ = \text{Hg}$$
$$\text{“ \ “ \ \ “ } \times \cdot 02709 = \text{HgCl}_2$$

Mercurous salts may be converted into the chloride by precipitation with sodium chloride.

Mercuric salts are changed into mercurous chloride by adding some sodium chloride, an excess of ferrous sulphate, and sodium hydrate to the solution. The sodium hydrate is added in sufficient quantity to make the fluid alkaline to test-paper. The mixture is allowed to stand for a short time, shaking frequently. As soon as the reaction is supposed to be completed, hydrochloric acid is added until the solution becomes clear, and the mercurous chloride white and free from iron. It is then filtered, washed thoroughly, and treated with potassium iodide and iodine, as above.

ESTIMATION OF MERCURY IN MERCURIC SALTS, ESPECIALLY IN MERCURIC CHLORIDE.

*By Oxidation of Ferrous Sulphate.**—The mercuric chloride is dissolved in water in a flask, a weighed amount of ferrous ammonium sulphate dissolved in water added, and sodium hydrate added until the ferrous oxide is precipitated and the solution decidedly alkaline. The mixture is then allowed to stand for a few minutes, shaking frequently. The flask must be kept full of hydrogen during the digestion to prevent oxidation of the ferrous oxide by the oxygen of the air. Hydrochloric or sulphuric acid is added to the mixture until the ferrous and ferric oxides are completely dissolved, leaving the mercurous chloride which forms perfectly white. The solution is then diluted to the mark, shaken, a portion filtered through a dry filter, measured out with a pipette, and the excess of ferrous salt estimated with bichromate. The reaction between the ferrous hydrate and the mercuric oxide in the alkaline solution is as follows:

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* Mohr, Titrirmethode.

$$2HgO + 2Fe(OH)_2 + H_2O = Hg_2O + Fe_2(OH)_6$$

Ferrous ammonium sulphate × ·5102 = Hg
" " " × ·6911 = $HgCl_2$

Mercurous salts may be converted into mercuric chloride by precipitating them as mercurous chloride by means of a solution of sodium chloride, washing the chloride, adding sodium hydrate, and passing chlorine through the solution. The solution is then acidified with hydrochloric acid and evaporated to expel the excess of chlorine.

Mercuric salts are converted into the chloride by evaporating with hydrochloric acid. In evaporating solutions of mercuric chloride, care must be taken not to allow them to boil, as in that case some of the chloride goes off with the steam. (Fresenius.)

*With Potassium Cyanide.**

The mercury must be present as mercuric chloride. Ammonia is added until a considerable amount of a white precipitate has formed (an excess of ammonia does no harm). A solution of potassium cyanide is then added until the precipitate redissolves and leaves the liquid perfectly clear. The strength of the standard potassium cyanide is best determined by titration in the same manner against a weighed amount of pure mercuric chloride. Since it decomposes slowly by keeping, the strength must be redetermined before each series of analyses. The temperature at which the titration is conducted should not be below 8° nor above 20°.

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* Hannay, Jour. Chem. Soc. 1873, 565.

.*With Potassium Iodide.**

When a neutral solution of mercuric chloride is added to a solution of potassium iodide, a colorless solution is formed until the proportion of mercuric chloride is to that of potassium iodide as 1 to 4. As soon as this proportion is exceeded, and more mercuric chloride added, mercuric iodide precipitates, which colors the solution red. The mercury must always be present as neutral mercuric chloride. It is necessary to add the mercuric chloride to the potassium iodide, since by reversing the process the same results are not obtained.

The standard solutions are—

Decinormal potassium iodide, made by dissolving 33·1974 gms. of the pure salt, and diluting to a litre.

Decinormal mercuric chloride, made by dissolving 13·5457 gms. pure mercuric chloride to a litre. An addition of about 30 gms. sodium chloride assists the solution of the mercuric chloride.

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* Personne, Comp. Rend. lvi. 63.

The mercuric chloride to be estimated is dissolved in water and added to an excess of the decinormal potassium iodide. The excess of potassium iodide is then found by adding $\frac{n}{10}$ mercuric chloride from a burette, until the red color makes it appearance.

$$\frac{n}{10} \text{ potassium iodide} \times \cdot 0100 = Hg$$
$$\text{" " "} \times \cdot 01355 = HgCl_2$$

ESTIMATION OF MERCURY BY SODIUM THIOSULPHATE.*

The standard solution is ½ the strength of that described on page 55, and contains 12·4043 gms. of the crystallized salt per litre.

Mercurous Nitrate.—When sodium thiosulphate is added to mercurous nitrate, the following reaction occurs:

$$Hg_2(NO_3)_2 + Na_2S_2O_3 + H_2O = Hg_2S + Na_2SO_4 + 2HNO_3$$

The solution, which must not contain mercuric salt, is diluted, heated, and the sodium thiosulphate run in from a burette, until no further precipitate is produced. The sulphide settles rapidly and the proper point is easily found.

$$\text{c. c. thiosulphate} \times \cdot 0200 = Hg$$
$$\text{" "} \times \cdot 0208 = Hg_2O$$

Mercuric Nitrate.—Sodium thiosulphate precipitates the mercury from mercuric nitrate, according to the following reaction:

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* Scherer, Lehrbuch der Chemie, 1, 513.

$$3Hg(NO_3)_2 + 2Na_2S_2O_3 + 2H_2O = 2HgS.Hg(NO_3)_2 + 2Na_2SO_4 + 4HNO_3$$

The solution is highly diluted, mixed with a little nitric acid, and the thiosulphate added until no further precipitate forms.

In order to distinguish the end of the reaction, Scherer recommends that the solution be diluted to a definite volume before the reaction is quite finished, and $\frac{1}{2}$ or $\frac{1}{3}$ the clear fluid taken out with a pipette, and the titration finished upon this portion. If any doubt exists, a second like quantity may be taken out and titrated in the same way. Multiply the number of c. c. of thiosulphate used with this fractional portion by two or three, as the case may be, and add it to the main quantity.

c. c. thiosulphate × ·015 = Hg or × ·0162 = HgO

Mercuric Chloride.—

$$3HgCl_2 + 2Na_2S_2O_3 + 2H_22O = 2HgS.HgCl_2 + 2Na_2SO_4 + 4HCl$$

The solution is acidified with hydrochloric acid, diluted largely, and heated nearly to boiling. Thiosulphate is then added as long as a white precipitate is formed. Care must be taken not to add an excess of thiosulphate, when the precipitate will become gray, or even black, and the analysis must be repeated. The filtering pipette may be used to determine the end of the reaction.

c. c. thiosulphate × ·0150 = Hg
" " × ·0162 = HgO

This method succeeds best with mercurous nitrate. As mercurous nitrate almost invariably contains mercuric salt, the process loses much of its value, not being applicable in such cases.

SILVER.

ESTIMATION BY PRECIPITATION AS CHLORIDE.

WHEN sodium chloride is added to an acid solution of silver, AgCl is thrown down. The precipitate being very insoluble in water and dilute acids, the results obtained are very sharp. The end of the reaction may be determined in three ways: 1st. By potassium chromate. 2d. By shaking the solution violently for some time, and allowing the silver chloride to subside before adding more of the reagent. 3d. Filtering off a small portion by means of the filtering pipette, Fig. 33, and testing the clear fluid. The second method is best in cases where the amount of silver is very nearly known, as in bullion, silver coin, etc. The first method is applicable only to neutral solutions, and the third may be used in either neutral or acid solution.

WITH CHROMATE AS INDICATOR,

the solutions needed are:

1. Decinormal sodium chloride.

5·85 gms. NaCl per litre.

If pure, perfectly transparent, and colorless rock-salt can be obtained, the solution may be made by dissolving the above amount, and diluting to a litre. The exact strength must, however, be determined by comparison with the silver solution to be described hereafter. If pure rock-salt is not obtainable, the sodium chloride may be purified by dissolving in water till the liquid is saturated, and then conducting a stream of hydrochloric acid gas through the liquid to saturation. The salt is deposited, while ferric and magnesium chlorides, etc., remain in solution. The precipitated salt is collected, dried between filter-paper, heated to incipient fusion in a platinum crucible, and the proper amount weighed out. The salt so prepared must not darken or show any color upon fusion and cooling, it must dissolve perfectly in water, and its solution must be neutral to test-paper, and give no precipitate with barium chloride.

2. Decinormal silver nitrate. The solution may be made either by dissolving 16·993 gms. silver nitrate, or by dissolving 10·793 gms. pure silver in nitric acid, evaporating to dryness, dissolving the residue in water, and diluting to a litre.

3. A saturated solution of potassium chromate. The potassium chromate used for this purpose must be perfectly free from chlorine.

The solution containing the silver must be neutral or faintly alkaline. If acid, it must be neutralized by means of a dilute solution of sodium carbonate free from chloride. Sodium chloride solution is added in excess, then two or three drops of the potassium chromate solution, and then the silver nitrate solution run in from a second burette. As long as any chlorine remains in excess, the drops of silver solution give at first a brick-red precipitate, which rapidly changes to white. The brick-red precipitate is silver chromate, which is, however, rapidly decomposed in a solution containing chlorine into silver chloride and chromic acid. As soon, however, as the chlorine is all precipitated, the fluid is colored by the red silver chromate formed, which does not again disappear. It is not so accurate to add chromate to a silver solution, and then sodium chloride, until the red color changes to white :

1st. Because the exact moment of the change from red to white is less easy to hit than that from white to red.

2d. The precipitated silver chromate, if allowed to stand any length of time, is less easily decomposed by a solution containing chlorine, and we are apt to overstep the proper point.

$$\text{c. c. } \tfrac{n}{10} \text{ silver nitrate} \times \cdot 010793 = \text{Ag}$$

BY AGITATING THE LIQUID.

The estimation may be made by precipitating the silver from the nitric acid solution, contained in a bottle with well-ground stopper, by means of the $\frac{n}{10}$ sodium chloride solution, shaking violently after each addition. The chloride collects in lumps, which sink to the bottom, leaving the supernatant liquid clear and fit for testing. During the shaking, the silver chloride must be protected from the action of light, which is done by slipping a black paper over it. When the precipitate has completely settled, leaving the liquid above perfectly clear, a drop of the $\frac{n}{10}$ sodium chloride is added, when, if silver is still in solution, a fresh precipitate makes its appearance. The method is more fully explained under the head of Silver Alloys.

BY THE FILTERING PIPETTE.

The solution of sodium chloride is run into the solution containing the silver, previously acidified with nitric acid, until both sodium chloride and silver nitrate produce a precipitate in a portion of the filtered liquid. If the point is overstepped in the first trial, 1 c. c. silver nitrate may be added, and then sodium chloride as before. When the burettes, etc., are properly graduated, and the analysis carefully executed, this method gives excellent results. It requires more time in execution than the chromate method, but the results obtained are rather nearer the truth.

ESTIMATION OF SILVER BY STARCH IODIDE (PISANI).

Applicable in presence of lead and copper, but not with mercury, tin, iron, manganese, antimony, arsenic, or gold.

The method is founded upon the fact that when starch iodide is added to a neutral solution containing silver, the silver is precipitated as iodide, and the blue color is destroyed as long as any silver remains in solution. As soon, however, as all silver precipitated, the iodide of starch colors the fluid

Standard Solution of Starch Iodide.

Weigh out 2 gms. iodine into a mortar, add 15 gms. starch, and mix, after adding 6 or 8 drops of water. The mass is transferred to a closely-stoppered flask, and heated on the water-bath for about an hour. Sufficient water is added to completely dissolve it. About ·01 gm. silver is weighed out, dissolved in nitric acid, evaporated to dryness, dissolved again in about 80 c. c. water, some precipitated and carefully washed calcium carbonate added, and the starch iodide solution run in from a burette, until the solution takes a greenish-blue tint from the iodide in excess. The ·01 gm. silver should require about 50 c. c. of the starch iodide solution.

The amount taken for an analysis should not contain more than ·01 to ·02 gm. silver. If more than this be present, the larger portion may be precipitated by means of $\frac{n}{10}$ sodium chloride, the silver chloride filtered off, and the remaining silver determined as above. The amount so found is then added to that which has been precipitated by the sodium chloride.

If preferred, the solution containing the silver may be diluted in a measuring-flask, and a part taken out for the titration by means of a pipette.

BY PRECIPITATION AS SULPHOCYANIDE.*

A soluble sulphocyanide added to silver solutions completely precipitates the silver as sulphocyanide, which is insoluble in acids. If a little ferric sulphate be added to the solution, the least excess of sulphocyanide is shown by the production of ferric sulphocyanide, which colors the liquid red.

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* Volhard, Jour. pr. Chem. [2] ix. 217; Jour. Chem. Soc. 1874, 919; Fres. Zeit. 13, 171; 16, 351.

The solutions used are:

Decinormal silver nitrate, the preparation of which has already been described.

Decinormal potassium sulphocyanide. The solution is best made by dissolving a portion of the salt in about 500 c.c. water, estimating the strength by titration against a measured volume of $\frac{n}{10}$ silver nitrate, and diluting until the solution is of the proper strength.

Solution of ferric sulphate. The salt must be free from chlorine. The solution may be made by dissolving one part ferric ammonium sulphate in 10 parts water.

5 c.c. of the ferric sulphate are added to the silver solution, and then $\frac{n}{10}$ sulphocyanide run in from a burette until the red color makes its appearance. The method is a very accurate one, and may be used with alloys containing less than 70 % copper. The sulphocyanide solution does not change by keeping.

$$\text{c. c. } \tfrac{n}{10} \text{ sulphocyanide} \times \cdot 010793 = \text{Ag}$$

ANALYSIS OF SILVER ALLOYS—COIN, ETC.

THE volumetric estimation of the silver in coin, bullion, etc., was introduced by Gay-Lussac into the European mints, and since then the process has, chiefly through the researches of Mulder, been brought to a high state of perfection. It is one of the most accurate as well as rapid volumetric estimations that we are acquainted with.

The content of silver of the alloy to be examined must be approximately known, and if this is not the case, we can easily ascertain it either by the method of cupellation, or by one of the volumetric methods before given.

The method is grounded upon the insolubility of silver chloride in weak nitric acid and water, and the ease and rapidity with which the precipitated chloride may be made to settle by violent agitation of the liquid containing it, leaving the supernatant liquid perfectly clear.

The solution of sodium chloride used for effecting the precipitation of the silver is of such strength that 100 c. c. at 15° C. precipitate exactly 1 gm. An amount of the alloy containing a little more than this amount of silver is weighed out, dissolved in nitric acid, 100 c. c. added, the liquid violently agitated for a short time, allowed to settle, and then the remainder of the silver precipitated by adding sodium chloride solution $\frac{1}{10}$ the strength of the above, in small portions at a time, shaking and allowing to settle after each addition until it ceases to produce a precipitate in the clear fluid. If we dissolve silver nitrate and sodium chloride, in the proportion of their molecular weights, in water, and mix the solution and agitate, we shall find that both silver nitrate and sodium chloride produce a precipitate in the clear solution, and that the amount of precipitate is the same, no matter which is used.

In the silver assay, we can therefore have the choice of three endings: 1. We may add sodium chloride until it ceases to produce a precipitate. 2. We may add sodium chloride until it and silver nitrate produce precipitates of equal amount. 3. We may add sodium chloride in excess, and then titrate back with solution of silver nitrate, equal in strength, until it ceases to give a precipitate. The second is the proper end reaction, since it marks the point when silver and chlorine remain dissolved in the fluid in exactly the proportions in which they unite to form silver chloride. It is, however, much more difficult to hit this point precisely than to find 1, and takes a much longer time. For this reason, the ending 1 is almost invariably used in the silver assay at the mints.

PREPARATION OF THE STANDARD SALT SOLUTION.

For this purpose, the salt used should be as pure as possible. Either transparent colorless rock-salt or salt purified by the process given on page 164 may be used. The salt must be finely pulverized, dried at 300° in the air-bath, placed under the desiccator until cool, and then the proper amount weighed out. It should not be allowed to stand in the air before weighing, as, according to Mulder, as much as 7 % of moisture is taken up in cool damp weather. The pure dry salt is weighed out and dissolved in the proportion of 5·4201 gms. (according to Mulder, 5·42215 ; to Mohr, 5·414 gms.) to a litre. The water must be pure distilled water free from organic substances. Rain-water will not answer, as it contains dissolved organic matter. Instead of weighing the salt used for making the solution, it is customary to make a saturated solution of pure salt, and measure out a sufficient quantity of this, and dilute with water. The solubility of sodium chloride in water is very slightly influenced by the temperature, and it is therefore possible to obtain a saturated solution which contains an unvarying amount of salt.

A saturated solution of pure salt has a specific gravity (15°) of 1·204, and contains 31·84 % of sodium chloride $\cdot\frac{5\cdot4201}{\cdot3184} = 17\cdot02$ c. c. is therefore the amount which is to be diluted to a litre. By actual experiment, Mulder found 17·13 c. c. as the proper amount. The saturated solution is prepared by allowing distilled water to stand in contact with an excess of pure salt for at least 13 days, shaking frequently. The clear fluid is then poured off and preserved in small carefully closed bottles to prevent evaporation. Each bottle should contain sufficient salt solution to make a stock bottle full of standard solution when it is diluted.

Decimal Salt Solution.

This should be precisely $\frac{1}{10}$ the strength of the standard solution, and may be made by diluting 100 c. c. to a litre. It is to be borne in mind that the solutions prepared as above are calculated for the ending 2, and if ending 1 be employed, a trifle more salt will be required.

Decimal Silver Solution.

When ending 2 is employed, it frequently happens that the neutral point is overstepped, and we must then add decimal silver solution until this is again reached. This solution is prepared by dissolving 1 gm. pure silver in a little nitric acid, and diluting to 1 litre.

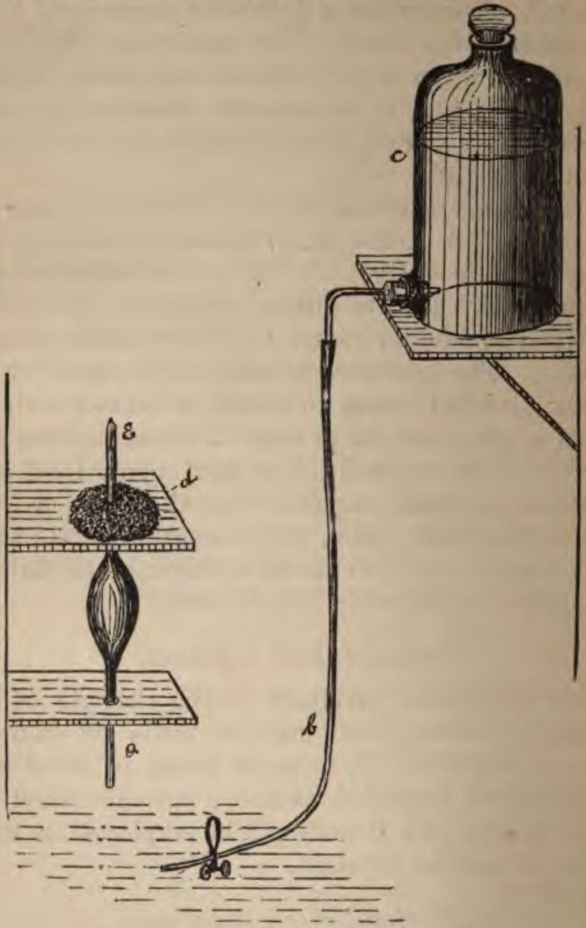

FIG. 35**.

THE APPARATUS.

The Pipette.—The form of pipette now in general use is shown in Fig. 35**. It has the advantage of great simplicity, and is rapidly filled and delivered. The upper part is drawn out to a fine point, and the lower part is cut off squarely and heated in the flame until a small aperture, 1 to 1½ mm. in diam. remains. The pipette is securely fastened in a heavy retort-holder, or fastened to the wall by a bracket, to prevent it from vibrating. The upper part is surrounded by a sponge to catch the fluid which overflows. The pipette is filled from below by means of the tube *b*. This is connected with a large jar or bottle containing the standard salt solution. It is slipped over the lower end of the pipette and the pinch-cock opened. The solution flows into the pipette until it is full, when the finger is placed upon the point *e*, the pinch-cock closed, and the tube slipped off. The pipette is now ready for delivering the fluid, which is done by simply removing the finger. It is evident that the accuracy of the whole process depends largely upon the accuracy with which a pipette of this kind may be made to deliver a given amount of liquid. Mulder has made careful experiments upon this point, and finds that the difference in weight of successive volumes of water at 15° delivered by such a pipette varies from 0–4 mgr. This exactness is only possible when the pipette is securely fastened to prevent vibration, and when care is taken to deliver in exactly the same way in every case. With a pipette held in the hand, Mulder observed differences of 20–40 mgr. in successive deliveries. To obtain the greatest degree of uniformity in the delivery, it is necessary that the pipette be firmly fastened, that it be perfectly clean, and that it be always delivered in the same way. It is best before use to rinse the pipette first with dilute sodium hydrate, then with hot nitric acid, then with water, and finally with some of the standard salt solution.

The apparatus used by Gay-Lussac for delivering the decimal salt solution consists of a tube, graduated in cubic centimetres, and passing through a cork which closes the bottle containing the solution. After 100 c. c. of the standard solution have been added to the assay, 1 c. c. of the decimal solution is added from the pipette, and, after the solution is shaken until clear, a second 1 c. c., and this process continued until an addition of 1 c. c. produces no precipitate. The number of c. c. used, less 1½, is the amount necessary for precipitation of the silver.

Mulder uses two pear-shaped vessels in completing the assay, one containing decimal salt, the other decimal silver solution. The vessels are drawn out below, and provided with two pinchcocks, the lower one provided with a screw for regulating the number of drops, and the upper one for stopping the flow of liquid completely. The opening of the delivery-tube is of such size that exactly 20 drops flowing from it are equal to 1 c. c. Accordingly, it is possible to measure the decimal solution to $\frac{1}{20}$ c. c., which is equivalent to only ·00005 gm. silver, and great accuracy is therefore attainable. The operation requires more time, however. Mohr uses a burette for holding the decimal solution, and, where but one assay at a time is made, this is certainly the most convenient, as it registers the amount of solution used ; but where a number of analyses are made at the same time, an equal number of burettes must be provided, and this is inconvenient, besides being expensive. Where rapidity is desired, and accuracy to $\frac{1}{1000}$ suffices, the first method is the best.

The Bottles.—These must be of white glass, containing 200–250 c. c., and with pointed stoppers, very accurately ground. They must be well annealed, and free from bubbles and flaws.

Shaking Apparatus.—Where a single assay is to be made, the bottle is covered with a cloth, after adding the standard solution, and shaken with the hand until the precipitate balls together, leaving the supernatant liquid clear. When ten assays are made at once, as is usual, a shaking apparatus is provided. The apparatus contrived by Gay-Lussac for holding the bottles is made of tinned sheet-iron, and contains ten compartments, into which the bottles fit, surrounding a central rod, to which they are soldered. The central rod terminates above and below in rings, to which thick rubber straps are fastened, which in turn are attached—the upper to a strong bracket projecting from the wall, and the lower one to a ring in the floor. The stoppers of the bottles are held in place by circular pieces of tinned iron, inserted in a hollow ring of the same material, and provided with springs at the back to keep them in place. This hollow ring has a hinge at one side, and may be turned completely over, so as to release the bottles. The apparatus, after the insertion of the bottles, is connected with the rubber bands, and gently shaken up and down for three or four minutes, when the solution will have become perfectly clear. Where many assays are performed, this shaking becomes very fatiguing, and, in the mints, is performed by attaching the shaker to the engine in a suitable way. The following extract from a private letter received from Mr. W. E. Du Bois, Chief Assayer in the United States Mint at Philadelphia, is interesting in this connection: "We began this humid assay in 1835, and for some time our agitator was moved by the two human arms, up and down. This was very fatiguing, even though it took but three or four minutes. We soon improved upon that, by having a wheel and leather cord, turned by a crank. But, as human nature is always devising expedients to get rid of work, we next concluded that the steam-engine, though not close by, might as well do the shaking; and so, by a connection of cords and pulleys, we made this second improvement; and it has worked well. The next advance was to get rid of the noise; and this was nearly dissipated by removing the tin cups or holders (ten in the circle), and substituting sole leather. Thus, you see, we are very ready to accept amendments; and in various ways these are suggested from time to time. If the engine happens to be still, we revert to the hand-crank, of course. And when only one assay is in progress, the elbow shake is the most convenient."

The apparatus employed bv Mulder for clearing the fluid consists of a board, carrying a wooden box at each end, provided with compartments for six bottles, or twelve in all. The board is 1 metre long and ·15 metre in width, and is fastened in the centre, by means of a hinge, to a triangular wooden block ·2 metre high, attached to a table so that the board may move up and down like a see-saw. The ends of the board have handles attached. The bottles are kept in place in the compartments by a strip of cloth to which is fastened a strip of vulcanized caoutchouc, and the two pieces are then drawn over the stoppers of the bottles, and fastened to the box at the ends with screws. This arrangement keeps the stoppers in place, holds the bottles firmly, and allows of their easy removal. The apparatus is very cheap, makes no noise, and is not tiresome to work.

Influence of Temperature.

The influence of temperature upon the end reaction is considerable. Mulder has shown that the difference between the 2d and 3d endings increases as the temperature rises. The difference is due to the differing solubility of silver chloride in the sodium nitrate which is formed, it being dissolved in greater quantity as the temperature rises, and hence requiring a larger quantity of sodium chloride to re-precipitate it.

As the ending 2 is found when precipitates of the same density are produced by both silver nitrate and sodium chloride, heat in this case exercises no influence except to make the precipitates rather more dense. The difference between the endings 1 and 2 is equal to

0·3 milligr. at 5°
0·4 “ “ 10°
0·5 “ “ 15°
0·6 milligr. at 20°
0·7 “ “ 24°

The temperature has also a decided influence upon the amount of solution delivered by the 100 c. c. pipette. As the temperature rises, the standard solution expands slowly, and, though the same volume of liquid is delivered by the pipette, it weighs less and contains less salt. Other things modify this in an important degree, however. The glass of the pipette expands at the same time, though in less amount, and partially corrects the error. In addition to this it is found that, as the temperature rises, the liquid adheres less strongly to the pipette, and a slightly increased volume is delivered. The actual difference produced by change of temperature in the amount of standard solution delivered by weight is shown in the following table of Mulder's:

Correction Table in Thousandths.

5°	+ 0·55	16°	− 0·125
6°	+ 0·5	17°	− 0·25
7°	+ 0·5	18°	− 0·4
8°	+ 0·45	19°	− 0.55
9°	+ 0·45	20°	− 0·7
10°	+ 0·4	21°	− 0·9
11°	+ 0·4	22°	− 1·1
12°	+ 0·3	23°	− 1·3
13°	+ 0.25	24°	− 1·525
14°	+ 0·125	25°	− 1·75
15°	0·		

If the standard solution have a temperature of 5°, for example, 100·055 c. c. of salt solutions will be delivered by the pipette, and the apparent value of the alloy, as shown by the assay, must accordingly be increased by ·00055 to give the true value. In the same way, the figures for degrees above 15° must be subtracted from the apparent to give the true value.

Influence of Other Metals upon the Precipitation of the Silver.

Copper, which is the metal most generally alloyed with silver, exercises no influence upon the result. Manganese, iron, zinc, cadmium, nickel, cobalt, arsenic, and palladium are also without influence. Tin is oxidized by nitric acid to stannic oxide, which does not settle well and makes it impossible to ascertain the end of the reaction. Where tin is present, the alloy must be dissolved in hot concentrated sulphuric acid. Antimony behaves in the same way, but the solution may be cleared by the addition of a little tartaric acid. Bismuth is precipitated upon the addition of the salt solution as oxychloride, but this is prevented by a little tartaric acid. Lead is only hurtful in considerable quantities. The alloy should be dissolved in sulphuric acid, or in nitric acid, and then sulphuric acid added to precipitate the lead.

With 1 gm. silver and 0·6 gm. lead dissolved in sulphuric acid, Mulder obtained 99·8875 silver, and with 1 gm. silver and 20 mgr. lead in nitric acid, and then sulphuric acid added, 1000 silver. If the lead is present in small quantity, no sulphuric acid need be added. Platinum, and also gold alloyed with silver in small quantity, dissolve in nitric acid and exercise no influence on the result. Of all metals mercury is the most objectionable, and must be removed before the process can be successfully used. Its presence is detected by standing the bottle containing the chloride in direct sunlight, when, if it be present, the chloride is but very slowly colored by the action of the light. The presence of mercury causes error in several ways: 1. It is difficult to clear the fluid by shaking. 2. Part of the mercury is dissolved as mercurous nitrate, and this is precipitated by the salt solution. 3. When the alloy is dissolved in hot nitric acid, mercuric nitrate is produced, which dissolves silver chloride in much greater quantity than sodium nitrate. In consequence, the difference between the endings 1, 2, and 3 is much greater when mercury is present than otherwise; and where ending 1 is used, false results are obtained. Levol adds an alkaline acetate to the alloy dissolved in hot nitric acid, and then proceeds in the usual way. The mercuric nitrate is in this way converted into mercuric acetate and sodium nitrate is produced. The results so obtained are better, but not altogether satisfactory. With 1 gm. silver and ·1 gm. mercury, adding 10 gm. sodium acetate, Mulder obtained 999·75 silver.

In a second example, with ammonium acetate the same result was obtained. The best plan is to heat alloys containing mercury until the mercury is completely driven off, then dissolve, and proceed in the usual manner.

Unequal Solidification of Silver Alloys.

Silver has a great tendency to form alloys of definite composition with other metals, and especially with copper and lead, which, in cooling, separate from the excess of either metal which may be present. This property is called, by Mulder, Liquation. Upon this property Pattinson's process for desilvering lead is founded. Silver forms a definite alloy with copper, having the formula Ag_3Cu_4, which contains 718·93 parts silver in 1000. If the alloy be of this composition, no separation takes place; but if more or less copper be present, it is found that the resulting bar of metal contains unequal quantities of silver in different parts. In the Dutch gulden (silver coin), which contains $945 \pm 1 \cdot 5$ parts silver in 1000, Mulder found differences of 1·72 thousandths between pieces taken from different parts of the coin. It is necessary, therefore, to exercise great care in taking a sample of an alloy if we wish to obtain the true silver value. The best plan is to melt the alloy, stir it thoroughly, take out a portion with a ladle, and pour into cold water. The cooling then is so rapid that the silver has no time to separate. The granulated pieces are flattened at first with a hammer and then by passing through rolls into sheets, from which pieces of proper size for the assay can be cut with scissors.

Pure Silver.

The strength of the standard salt solution is always found by titration against pure silver. Silver coin is dissolved in nitric acid, the solution filtered, diluted, and precipitated by the addition of hydrochloric acid. The flask is covered and allowed to stand until the supernatant liquid becomes perfectly clear, when it is poured off. Distilled water is then added, and the silver chloride washed by decantation until sulphuretted hydrogen produces no brown color in the washings. The moist chloride is placed in a lamp-chimney, over one end of which a piece of bladder is tightly fastened. This is placed in a vessel containing dilute sulphuric acid. A silver wire soldered to a piece of amalgamated zinc is placed in the silver chloride, and the zinc in the dilute sulphuric acid in the outer vessel. A galvanic current is immediately produced, and the chloride is reduced to the metallic state. When the reduction of the silver is complete, which occupies 24–48 hours, the finely-divided metallic silver is digested with hot dilute sulphuric acid, and then washed repeatedly by decantation until perfectly free from sulphuric acid. The silver still contains a notable quantity of chloride, but this makes no difference. It is mixed while still moist with a little pure sodium carbonate, borax, and sodium nitrate, and dried. A porcelain crucible is placed within a larger Hessian one, and the space between them filled with sand mixed with a little powdered borax, which melts in the fire and keeps the sand in place. The crucibles are placed in the fire, and as soon as the inner one becomes red hot, the dried silver powder is filled in, the crucible covered and allowed to remain in the fire until the silver is in quiet fusion. It is taken out, and the silver poured into a well-dried mould made of pipe-clay. The bar so obtained is cleaned from any adhering solid particles by scouring, and beaten and rolled into sheet form for use.

Pure Nitric Acid.

The acid used for dissolving the silver must be free from chlorine, and may be prepared from impure acid by distilling with a little potassium bichromate. The hydrochloric acid is then converted into chlorine, which passes over with the first distillate, and the remaining portion is perfectly pure.

Pure Sodium Chloride.

In addition to the method given on page 164, the following process given by Mohr may be used for purifying sodium chloride. Dissolve the crystals in water, add a little baryta water, and then sodium carbonate in excess, and evaporate the filtered solution to crystallization. Redissolve in water and recrystallize. Pure sodium chloride may also be obtained by adding pure hydrochloric acid to a solution of pure sodium carbonate until the fluid reacts neutral, evaporating to crystallization and recrystallizing.

Determining the Strength of the Standard Solution.

1·002 to 1·004 gm. of pure silver is very carefully weighed out and dissolved in 5 c. c. nitric acid, in one of the bottles described on page 175. The bottle is placed upon a sheet-iron plate in an inclined position, the stopper being removed. The plate is gently heated by a row of Bunsen burners. The bottles must be very carefully annealed or they will not stand this treatment. When solution is complete, the nitrous fumes are blown from the bottle either with the breath or with a small pair of bellows to which a bent tube is attached, and the bottle is then allowed to cool. When it has reached the temperature of the atmosphere, it is placed in a tin case, brought under the 100 c. c. pipette, and the contents allowed to flow in. The stopper is dipped in distilled water, inserted, and the bottle is then covered with a black cloth and shaken for 3 or 4 minutes, until, upon standing for a few seconds, the supernatant fluid becomes perfectly clear. The chloride adhering to the stopper is then shaken down by imparting a circular motion to the fluid, and the stopper is taken out. The drop of fluid adhering to the point is removed by touching against the neck of the bottle. If the standard solution be of such strength that 100 c. c. precipitate exactly 1 gm. silver, there will still remain in solution the excess over 1 gm. Fill the pipette-tube with decimal salt solution, and placing the point against the neck of the bottle, allow one or two drops to run in. If a precipitate is produced, it shows that silver still remains, and that more salt solution must be added. From the density of the precipitate produced by the first drop of salt solution, we can tell by practice about how much is still necessary, and this amount is then added, the liquid shaken, and the supernatant fluid tested as before. This is repeated until a drop of the decimal solution produces no precipitate, when the assay is finished. If the first drop of decimal salt solution produces no precipitate, salt is already in excess. A few c. c. of decimal silver solution must then be added until silver is in excess, and the process then proceeded with as before. Suppose 1·004 gm. pure silver require 100 c. c. standard salt solution, and 3 c. c. decimal solution. It is then a little too strong, and 100 c. c. is equal to $\frac{100 \cdot 4}{100 \cdot 3} = 1 \cdot 000997$ gm. silver. The strength of the standard solution should be determined in this way at the beginning of each day's work, and as the conditions of temperature, etc., will then be the same in the test assay and the subsequent assays, no correction need be applied. Before using any of the standard solution, the vessel containing it must be shaken so as to wash down any condensed vapor adhering to the sides.

The Assay of Alloys.

Assays are usually made in sets of 10, and carried through together. The amount of silver in the alloy must be approximately known, and is found either by cupellation or by means of normal salt solution, with potassium chromate as indicator.* In the latter case, lead and bismuth must be absent. An amount of the alloy containing a little more than 1 gm. silver is then weighed out, dissolved in nitric acid, and the assay completed in the same way as in the test assay, with 1 gm. silver. Suppose the alloy contains about 900 parts silver, then

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* Volhard's method may also be used.

900 : 1000 :: 1 : x; x=1·1111; 1·1111 is, therefore, the amount of alloy which contains 1 gm. silver, and a little more than this, say 1·115, should be weighed out for the assay.

For further information upon this interesting subject, the student is referred to the following works: Gay-Lussac's, "Chaudets' L'Art de l'Essayeur;" Mulder's "Silber-Probirmethode," German translation by Grimm, Leipzig, 1859; Regnault's Chemistry; Watts' Dictionary of Chemistry; and Mitchell and Crookes' work on Assaying.

GOLD.

BY OXALIC ACID AND PERMANGANATE.

THE gold must be present in the form of chloride. When gold chloride is mixed with oxalic acid in solution, the following reaction takes place:

$$2AuCl_3 + 3H_2C_2O_4 = 2Au + 6HCl + 6CO_2$$

The gold precipitates in the metallic form, and a quantity of oxalic acid corresponding to it is decomposed, carbon dioxide, which escapes, and hydrochloric acid being formed. The oxalic acid, either a measured volume of a solution or a weighed amount of the solid acid, is added, and the solution allowed to stand 18 to 24 hours. The solution is then made up to 300 c. c. in a flask, 100 c. c. taken out with a pipette, and the excess of oxalic acid found by means of permanganate.

Oxalic acid ($C_2H_2O_4 + 2H_2O$) × 1·0405 = Au

c. c. normal oxalic acid × ·06556 = Au
" " " " × ·10101 = $AuCl_3$

Oxalic acid ($C_2H_2O_4 + 2H_2O$) × 1·6034 = $AuCl_3$

NITROGEN COMPOUNDS.

AMMONIA.

THE percentage of ammonia in a watery solution of the gas may be found by taking the specific gravity and comparing with the following table:

TABLE.

Showing the percentage of Ammonia (NH_3) contained in solutions of different specific gravity. Temp. 14° (Carius).

Specific Gravity.	Ammonia, per cent.	Specific Gravity.	Ammonia, per cent.	Specific Gravity.	Ammonia, per cent.	Specific Gravity.	Ammonia, per cent.
0·8844	36	0·9052	27	0·9314	18	0·9631	9
0·8864	35	0·9078	26	0·9347	17	0·9670	8
0·8885	34	0·9106	25	0·9380	16	0·9709	7
0·8907	33	0·9133	24	0·9414	15	0·9749	6
0·8929	32	0·9162	23	0·9449	14	0·9790	5
0·8953	31	0·9191	22	0·9484	13	0·9831	4
0·8976	30	0·9221	21	0·9520	12	0·9873	3
0·9001	29	0·9251	20	0·9556	11	0·9915	2
0·9026	28	0·9283	19	0·9593	10	0·9959	1

By Normal Acid.

Litmus is added and then normal acid run in until the color changes.

c. c. normal acid × ·014044 = N
" " " × ·017044 = NH_3

Ammonia in combination may be estimated by distilling the substance containing it with potassium or sodium hydrate, and receiving the ammonia which distils over in a known volume of normal or decinormal acid. After the distillation is completed, the excess of acid over that required to neutralize the ammonia is found by titrating back with normal or decinormal ammonium hydrate. The distillation is performed in the flask A, Fig. 36, which contains the ammonium salt in solution; *b* contains strong solution of sodium hydrate. The flask B contains a measured quantity of normal hydrochloric acid, which is poured in through the tube *c* containing fragments of glass. The pinch-cock upon *b* is opened, which allows the sodium hydrate to run into the flask, and the solution is then gently boiled until all the ammonia is driven over and absorbed by the normal acid. Care must be taken not to heat too strongly, or the solution will foam up and pass into the flask B. After the distillation is completed, the acid adhering to the broken glass in *c* is washed into the flask, litmus added, and the excess of acid found by titrating with normal ammonium hydrate.

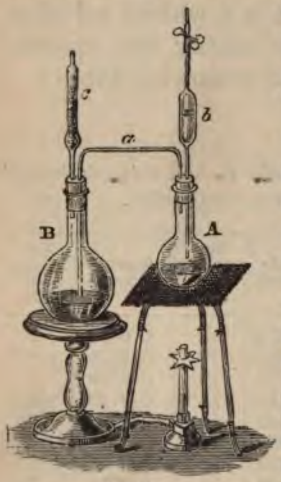

FIG. 36.

The nitrogen in most organic substances may be converted into ammonia and estimated as above by heating in a glass tube with soda lime (Will and Varrentrapp's method), receiving the ammonia given off in a bulb containing a known volume of normal hydrochloric acid, estimating the excess of acid with normal ammonium hydrate.

When a substance in which ammonia is contained contains also nitrogenous organic matter, boiling with sodium hydrate will not answer for estimating the ammonia, since boiling alkali in contact with nitrogenous matter produces ammonia. In such cases it becomes necessary to use calcined magnesia instead of solution of sodium hydrate for expelling the ammonia. If the nitrogen as well as ammonia is to be determined in a substance containing both, a portion is boiled with magnesia for some time and the ammonia determined as above. A second portion is ignited with soda lime in a combustion tube, and the total ammonia determined. The difference between the two determinations gives the nitrogen existing in combination as azotized organic matter. In neutral ammonium salts, the ammonia may also be estimated as follows: Boil the solution in a beaker covered with a watch-glass with an excess of normal sodium hydrate, until the steam no longer turns red litmus paper blue. In this way the ammonia is all driven off, and the acid combines with an equivalent quantity of the sodium hydrate. The excess of sodium hydrate is then estimated by back titration with normal acid.

AMMONIUM CARBONATE

Is estimated by dissolving in water, adding an excess of normal acid, and titrating back with normal alkali, after boiling to expel the carbon dioxide.

AMMONIUM CHLORIDE.

The amount of ammonium chloride in watery solutions may be found by taking the specific gravity and comparing with the following table:

TABLE.

Showing the percentage of Ammonium Chloride in solutions of different specific gravity. Temp. 15°. Water at 15°=1. *

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00316	14	1·04325
2	1·00632	15	1·04524
3	1·00948	16	1·04805
4	1·01264	17	1·05086
5	1·01580	18	1·05367
6	1·01880	19	1·05648
7	1·02180	20	1·05929
8	1·02481	21	1·06204
9	1·02781	22	1·06479
10	1·03081	23	1·06754
11	1·03370	24	1·07029
12	1·03658	25	1·07304
13	1·03947	26	1·07375

By Decinormal Silver Nitrate.

The substance must contain no other chloride. Three drops of a saturated solution of potassium chromate are added to the neutral solution, and $\frac{n}{10}$ silver nitrate is run in from a burette until the red color of silver chromate is permanent. (See Chlorine.)

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* **Gerlach, Specifische Gewichte der Salzlösungen.**

c. c. $\frac{n}{10}$ silver nitrate $\times \cdot 0014 = N$
" " " " $\times \cdot 0017 = NH_3$
" " " " $\times \cdot 00535 = NH_4Cl$

Ammonium hydrate and carbonate may be converted into chloride by supersaturating with hydrochloric acid, and evaporating to hard dryness on the water-bath. Other ammonium salts may be converted into chloride by distilling with sodium hydrate, receiving the ammonia given off in dilute hydrochloric acid, and evaporating to dryness as above. The nitrogen in organic substances may be estimated by combustion with soda lime in a glass tube; the ammonia is received in hydrochloric acid, and, after the combustion is completed, this is evaporated to dryness, filtered if necessary, and the chlorine estimated by $\frac{n}{10}$ silver nitrate as above.

ESTIMATION OF AMMONIA WITH BROMIZED SODIUM HYPOCHLORITE.*

The method is based upon the fact that ammonia is decomposed by a solution of sodium hypochlorite to which free bromine has been added, nitrogen being set free. The excess of solution over that required to decompose the ammonia is found by titrating with $\frac{n}{10}$ sodium arsenite.

Preparation of the Bromized Hypochlorite.—One part crystallized sodium carbonate is dissolved in 15 parts water, and chlorine passed through the cold solution until it is completely saturated. Sufficient sodium hydrate is then added to make the solution feel slippery when rubbed between the fingers; and just before the solution is to be used, enough bromine is added to give it a lemon-yellow color. The solution is diluted until it nearly corresponds in strength with the $\frac{n}{10}$ sodium arsenite. The strength of this solution is found by measuring out a portion and adding $\frac{n}{10}$ sodium arsenite until a drop taken out and placed upon paper saturated with a solution of starch and potassium iodide (see estimation of Hypochlorites) no longer produces a blue stain.

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* Fres. Zeitschrift für An. Chemie, 3, 64.

The analysis is made by adding a slight excess of the bromized hypochlorite to the ammonia salt, and estimating the excess by $\frac{n}{10}$ arsenite as above. Knowing the value of the bromized solution in $\frac{n}{10}$ arsenite, the amount of ammonia or nitrogen may be calculated from the following data:

c. c. $\frac{n}{10}$ arsenite $\times \cdot 0004666 = N$
" " " $\times \cdot 0005666 = NH_3$

The method is not remarkable for accuracy, and possesses no advantage over the alkalimetric method.

NITRIC ACID.

THE specific gravity of the acid being known, the percentage amount can be found by the following table:

TABLE.

Showing the amount of Nitric Acid (HNO_3) *contained in solutions of different specific gravity. Temp.* 15° (*Ure*).

HNO_3 per cent.	Specific Gravity.	HNO_3 per cent.	Specific Gravity.	HNO_3 per cent.	Specific Gravity.
100	1·5000	66	1·3783	33	1·1895
99	1·4980	65	1·3732	32	1·1833
98	1·4960	64	1·3681	31	1·1770
97	1·4940	63	1·3630	30	1·1709
96	1·4910	62	1·3579	29	1·1648
95	1·4880	61	1·3529	28	1·1587
94	1·4850	60	1·3477	27	1·1526
93	1·4820	59	1·3427	26	1·1465
92	1·4790	58	1·3376	25	1·1403
91	1·4760	57	1·3323	24	1·1345
90	1·4730	56	1·3270	23	1·1286
89	1·4700	55	1·3216	22	1·1227
88	1·4670	54	1·3163	21	1·1168
87	1·4640	53	1·3110	20	1·1109
86	1·4600	52	1·3056	19	1·1051
85	1·4570	51	1·3001	18	1·0993
84	1·4530	50	1·2947	17	1·0935
83	1·4500	49	1·2887	16	1·0878
82	1·4460	48	1·2826	15	1·0821
81	1·4424	47	1·2765	14	1·0764
80	1·4385	46	1·2705	13	1·0708
79	1·4346	45	1·2644	12	1·0651
78	1·4306	44	1·2583	11	1·0595
77	1·4269	43	1·2523	10	1·0540
76	1·4228	42	1·2462	9	1·0485
75	1·4189	41	1·2402	8	1·0430
74	1·4147	40	1·2341	7	1·0375
73	1·4107	39	1·2277	6	1·0320
72	1·4065	38	1·2212	5	1·0267
71	1·4023	37	1·2148	4	1·0212
70	1·3978	36	1·2084	3	1·0159
69	1·3945	35	1·2019	2	1·0106
68	1·3882	34	1·1958	1	1·0053
67	1·3833				

BY NORMAL ALKALI.

Litmus is added to the diluted acid, and normal alkali run in until the color changes.

c. c. normal alkali × ·063044 = HNO_3
" " " × ·054044 = N_2O_5

Nitric acid may be liberated from nitrates and estimated as above by distilling the nitrate with sulphuric acid. For 1 gm. nitrate, 10 c. c. of water and 5 c. c. strong sulphuric acid are required. The nitrate is poured into a tubulated retort, which is connected with a receiver containing normal alkali. The diluted sulphuric acid is then poured into the retort, and the retort buried in sand. The distillation is kept up for three or four hours, at a temperature not exceeding 170° and not less than 160°. If the nitrate contains chloride, some silver sulphate or moist silver oxide is added. After the distillation is complete, the receiver is washed out, and the excess of alkali found by normal acid.

The distillation may be performed in a partial vacuum,* by connecting the retort air tight with a receiver having two tubulures. Place the normal alkali, diluted with water, in the receiver, and the dilute sulphuric acid in the retort. Heat the contents of both vessels to boiling, with the tubulures open. When the air is expelled from both vessels, drop the nitrate contained in a small glass tube through the tubulure of the retort, quickly insert the stopper, and then insert the stopper of the receiver and take away both lamps. The retort is placed upon a water-bath, and, as the nitric acid will all go over at this temperature in the vacuum, the distillation may be left to take care of itself. The greatest advantage obtained by this process is, that there is far less danger of sulphuric acid going over with the nitric acid than when the temperature is raised to 170°.

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* Finkener, Zeit. Anal. Chem. 1, 309.

ESTIMATION BY OXIDATION OF FERROUS SALTS.

When free nitric acid is added to a ferrous salt, it is oxidized to the ferric state, and all the nitric acid is converted into nitric oxide.

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + N_2O_2 + 4H_2O$$

Weigh or measure the substance into a flask, add some hydrochloric acid and a weighed amount of ferrous ammonium sulphate, or a measured volume of the decinormal solution. The flask is heated on the water-bath for fifteen minutes, while a stream of hydrogen or carbon dioxide is passing through it; it is then boiled over the lamp until the solution has a clear yellowish color, and all N_2O_2 is driven off, then allowed to cool, and the excess of ferrous salt estimated by bichromate.

Instead of estimating the excess of ferrous salt, the amount of ferric salt produced may be estimated by one of the methods described under Iron.

BY CONVERTING INTO NITRIC OXIDE, AND RECONVERTING INTO NITRIC ACID.*

The following description of this process is taken from Fresenius's "Quantitative Analysis" (New York, 1871):

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* Annal. de Chim., 3 ser., tom. 40, 479; Jour. f. Prakt. Chem. 62, 142.

"The following method, employed by Schlösing, more particularly to determine nitric acid in tobacco, and which affords this very important advantage, that it may be used in presence of organic matter, has successfully passed through the ordeal of numerous and searching experiments.

"The dissolved nitrate is introduced into a flask of 400 c. c. capacity, Fig. 37, which is connected, by means of an India-rubber stopper, with a narrow glass tube *a*, which is joined by means of a rubber tube 8 cm. long with another glass tube that is again terminated at *d* by a piece of rubber tube. At *c* a pinch-cock is placed. The solution of the nitrate, which must be neutral or alkaline, is heated to boiling, *d* being stationed in a beaker of water, until the atmospheric air is perfectly expelled from the apparatus. When the vapors that pass over completely condense in *d*, the pinch-cock *c* is closed and the lamp is removed. Water immediately rises in the tube and fills it entirely to *c*. Shortly the vapors in the flask condense, as is shown by the collapse of the rubber tube at *c*. At this moment the tube *d* is removed from the water and dipped in a glass containing a solution of protochloride of iron in hydrochloric acid.

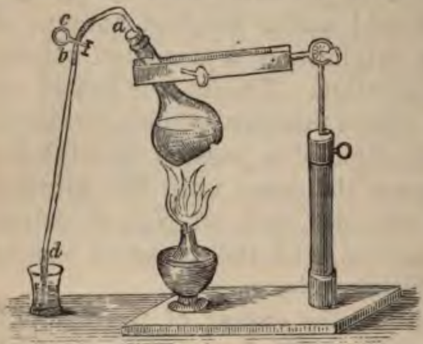

FIG. 37.

"The pinch-cock is cautiously opened, so as to allow the protochloride to enter the flask slowly. When sufficient of the iron solution has been introduced, the pinch-cock is closed, and *d* is brought into a vessel of hydrochloric acid, and portions of this are made to enter the flask in the same manner repeatedly, until the tubes are completely washed of all protochloride. In these operations, as in all the subsequent transfers, it is needful to exclude all traces of air, which is easy, provided the drop of liquid that hangs to *d*, when it is carried from one liquid to another, is not allowed to fall off. Finally, the tube is rinsed once by allowing the boiling water to recede, and then, the cock being closed, the tube *d*, still full of water, is passed into the lateral tubulure of the receiver, Fig. 38, which stands immersed in mercury.

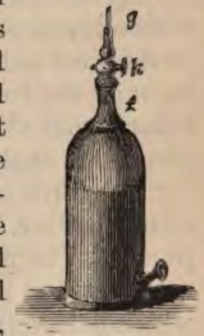

FIG. 38.

"The flask is again gently heated, and its contents immediately boil with violent thumping. The solution becomes black, and shortly the collapsed rubber tube at *c* shows that there is interior pressure. As soon as this is evident, open the cock and allow the nitric oxide gas to pass over into the receiver.

"The receiver, Fig. 38, has a rough-ground neck, which is connected by rubber *f* with a brass cock;* the latter is likewise joined by rubber to a short glass tube *g*. Into this receiver, the cock being open, some water, free from air by long boiling, and cooled in a closed vessel, is introduced by a tall funnel-tube fitted into the tubulure, and then mercury is poured in until it fills the vessel up to the lower edge of the rubber *f*. In this operation, the cock and small tube *g* should be over-filled with the water previously added. The receiver is thus empty of all air, and stands with the tubulure covered with mercury, as in Fig. 39.

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* Such receivers (Bunsen's gasometer) may be procured with a glass stop-cock.

"By means of a pipette, having a narrow rubber tube slipped over its tip, about 50 c. c. of thick and well-boiled milk of lime are passed into the receiver through the tubulure. This is to absorb the hydrochloric acid which boils over from the flask, and the receiver is shaken to facilitate the absorption.

"The nitric oxide, expelled from the flask by continual boiling, gathers in the receiver in a state of purity. The period of its complete transfer is exactly marked by the deposition of the milk of lime, which is thrown into agitation by the passage of a permanent gas, but quietly condenses or absorbs steam and hydrochloric acid. The completion of the reaction is also indicated, in case pure nitrates are employed, by the liquid in the flask assuming the color of pure sesquichloride of iron. When dark vegetable extracts are under analysis, this indication is not offered.

"Should the nitric oxide come off in quantity greater than the receiver can contain at once, the cocks are closed, and the lamp is removed from under the flask. The receiver is then emptied, as is subsequently described, charged anew with water, mercury, and milk of lime, reconnected, and the boiling resumed. When the nitric oxide has been completely collected in the receiver, it must be transferred to a second flask, to be converted into nitric acid.

"This flask, Fig. 39, arranged like the one already described, contains at first about 100 c. c. of pure water, which is boiled to expel all atmospheric air, and while still boiling vigorously, is connected with the receiver by passing the end of the tube *x* over the glass tube *g* of the latter. The lamp is then removed, and when collapse of the rubber tube takes place, the brass stop-cock of the receiver is slightly and cautiously opened, and the gas allowed to recede into the flask until the milk of lime reaches the lower edge of *f*. The cock is then closed, and the last portions of nitric oxide are rinsed into the flask by passing into the receiver a few (20–30) c. c. of pure hydrogen (washed by passing through oil of vitriol and milk of lime), and allowing this to recede in the same way. This rinsing is repeated three or four times. The rubber tube is now closed by a

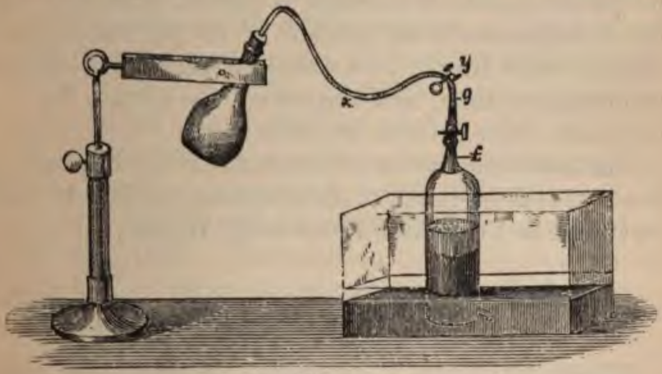

FIG. 39.

pinch-cock at *y*, and disconnected from the receiver. It is then united in the same manner with a gas-holder containing pure oxygen under pressure, and the gas is made to enter the flask. It is absorbed with the appearance of red fumes and the formation of nitric acid. After half an hour or so, the flask being occasionally shaken, the nitric acid is dissolved in the water of the flask, and may be estimated by a standard alkaline solution.

"Frühling and Grouven, who applied this method to the estimation of nitrates in plants, extracted the dried vegetable with alcohol of 50 per cent, evaporated the solution to a small volume, precipitated with caustic lime, and employed the filtrate for the analysis. For details, see their paper."*

An interesting series of experiments by Eder upon the different methods of determining nitric acid will be found in Fresenius, Zeitschrift, 16, 267.

BY CONVERTING INTO AMMONIA.

When hydrogen is generated in a solution containing nitric acid, ammonia and water are formed.

$$KNO_3 + 8H = NH_3 + KOH + 2H_2O$$

For generating the hydrogen, Nesbit uses zinc in cold dilute acid solution. Shulze platinized zinc in alkaline solution ; Harcourt and Siewart, zinc and iron filings in alkaline solution ; and Thorpe uses zinc covered with precipitated copper in neutral solution. If the reduction be effected in acid solution, the solution must be kept dilute and cold, and small quantities of acid added at a time. When hydrogen ceases to come off, the remaining zinc is carefully washed, the whole liquid distilled with sodium hydrate, and the ammonia in the distillate estimated by normal acid.

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* Versuchs Stationen, ix. 14.

If the reduction is to be made in neutral solution, pieces of zinc covered with finely-divided metallic copper (prepared by placing granulated zinc in a warm solution of copper sulphate, allowing to stand for ten minutes, and washing the zinc by decantation) are added to the dilute solution of the nitrate, which is gradually heated to boiling, and distilled for about an hour. The distillate contains the ammonia, which is estimated by normal acid.

When the estimation is to be made in alkaline solution, 1 gm. of the nitrate, 4 gms. iron filings, 8–10 gms. zinc filings, and 16 gms. solid potassium hydrate are taken. The solution is gently heated for about half an hour, and then boiled until all ammonia is driven over.

c. c. normal acid $\times \cdot 063044 = HNO_3$
" " " $\times \cdot 054044 = N_2O_5$

The process is not remarkably accurate. Under certain circumstances of dilution and temperature, nitric, and sometimes also nitrous, oxide escapes, and the reduction is seldom complete.

Alkaline nitrates may be estimated by mixing them with an equal weight of pure starch in fine powder, and six times as much sodium chloride, and heating in a covered crucible until deflagration takes place. The nitrates are converted into carbonates, which may be estimated by treating the black residue with water, and titrating the alkaline carbonate in the filtrate by means of normal acid. The carbonate is partly volatized by the heat, however, which makes the results too low; and if sulphates be present, they are reduced to sulphides, which make the results too high.

Neutral metallic nitrates whose bases are precipitable by sodium hydrate or carbonate may be estimated by treating them with an excess of normal solution, and estimating the excess. (See page 43.)

NITROUS ACID.

NITROUS acid, in contact with potassium permanganate in dilute solution, is oxidized to nitric acid:

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

A large quantity of distilled water is placed in a flask, slightly acidified with dilute sulphuric acid, and a few drops of centinormal permanganate run in so as to color the fluid perceptibly. The nitrous acid, or nitrite dissolved in water, is then added, and permanganate run in until nearly all the nitrous acid is oxidized. More sulphuric acid is then added, and permanganate again until the same color is produced as at first. The solution must not contain more than ·009 gms. nitrous acid per litre after dilution. As the solution is so dilute, it becomes necessary to proceed as above, otherwise the quantity of permanganate used to color the solution would introduce an appreciable error.

The amount of lower oxides of nitrogen contained in red nitric acid may be estimated as nitrous acid by this method. The red acid is measured out in a pipette, and poured from this into a large quantity of water colored by permanganate. The point of the pipette should be placed below the surface of the water. Permanganate is then added until the same color as at first is again produced.

c. c. $\frac{n}{100}$ permanganate × ·000235 = HNO_2
" " " × ·00019 = N_2O_3

The strength of the $\frac{n}{100}$ permanganate may be determined by titration against a weighed amount of pure silver nitrite, which is prepared as follows: Pure potassium nitrate is fused at a strong red heat for some time, allowed to cool, dissolved in hot water, and the greater part of the undecomposed nitrate crystallized out; the potassium nitrite being very soluble, remains in the mother liquor. A small portion of the mother liquor is then treated with a few drops of silver nitrate. If the precipitate is brown or yellowish, the heat has been too intense, and a portion of the nitrite been decomposed. Add nitric acid to the rest of the mother liquor until a portion tested with silver nitrate gives a white precipitate, and then add silver nitrate until a precipitate ceases to form. The precipitate is washed with a little cold water, dissolved in boiling water, and recrystallized once or twice. The crystals obtained have the composition $AgNO_2$.

CYANOGEN.

When silver nitrate is added to the solution of an alkaline cyanide, the following reaction takes place:

$$2KCN + AgNO_3 = KNO_3 + KCN,AgCN$$

The potassium silver cyanide formed is soluble. As soon, however, as the smallest quantity of silver nitrate beyond that required to perform the above reaction is added, the double cyanide is in turn decomposed, $KCN,AgCN + AgNO_3 = KNO_3 + 2AgCN$, and a precipitate of silver cyanide immediately appears. The cyanogen to be estimated must be in alkaline solution: $\frac{n}{10}$ silver nitrate is added with constant shaking until a faint permanent precipitate remains. 1 molecule silver nitrate = 2 molecules cyanogen, or hydrocyanic acid.

c. c. $\frac{n}{10}$ silver nitrate × ·0052 = CN
" " " " × ·0054 = HCN
" " " " × ·01304 = KCN

Double cyanides, or cyanides insoluble in dilute alkali, cannot be determined as above, and it becomes necessary to decompose them by means of hydrochloric acid in the flask, Fig. 40.*

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* Carl Mohr, Liebig's Annalen, 95, 110.

If all the hydrochloric acid were added at once, the hydrocyanic acid produced would be partially decomposed into formic acid and ammonia. For this reason, the hydrochloric acid to be used for the decomposition is sucked into the pipette, and the cyanide, together with some water, is placed in the flask. The water in the flask is then heated to boiling, and the hydrochloric acid allowed to flow in slowly, drop by drop. In this way the hydrocyanic acid formed by each drop of hydrochloric acid distils over immediately with the vapor of water, and is condensed by means of the Liebig condenser.

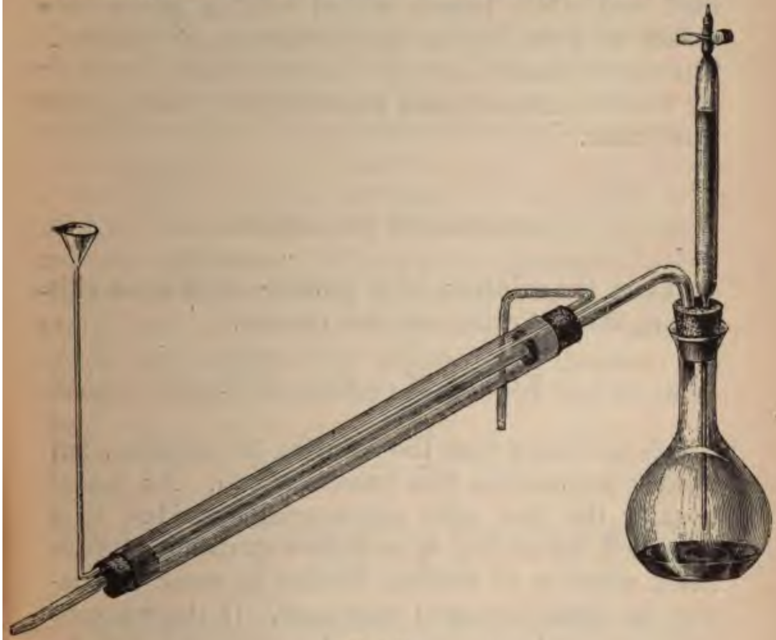

FIG. 40.

The hydrocyanic acid produced is received in a dilute solution of potassium hydrate, and the amount of cyanogen found by $\frac{n}{10}$ silver nitrate.

Instead of adding silver nitrate to the solution until a precipitate begins to form as above, the solution containing the cyanide may be slightly acidified and silver nitrate added until a precipitate ceases to form, as in the estimation of chlorine. The silver cyanide, like the chloride, balls together by violent agitation, and settles rapidly, leaving the fluid clear.

ESTIMATION BY IODINE.

When the solution of a cyanide is treated with iodine, the following reaction occurs :

$$KCN + 2I = KI + CNI$$

It is necessary that the solution be alkaline, but it must not contain free caustic alkali. As this is usually the case with commercial cyanides, it is remedied by adding a sufficient quantity of saturated solution of carbon dioxide in water, to convert the alkali into acid carbonate. If the water be saturated under pressure (soda water), less will be required. Starch is added to the solution, and iodine run in until the blue color appears. The solution should be dilute, about 3–4 gms. cyanide to a litre.

c. c. $\frac{n}{10}$ iodine × ·0013 = CN
" " " × ·003259 = KCN

ESTIMATION BY SOLUTION OF COPPER SULPHATE.

The method is the exact reverse of the method for copper. A solution of copper sulphate is added to the ammoniacal solution of the cyanide, until the blue color at first produced by the copper no longer disappears. If the operation is performed in a porcelain dish, it is easy to hit the exact point.

As in the estimation of copper, the reaction varies with the dilution, temperature, and amount of free ammonia, and the results are by no means exact unless the standardizing of the copper solution and the analysis are performed under precisely similar conditions. Whether the cyanogen be estimated by silver nitrate, iodine, or copper sulphate, sulphides must first be removed. This may be done by adding some freshly precipitated and washed lead carbonate to the solution, and filtering.

POTASSIUM FERROCYANIDE AND FERROCYANIDES.

THE amount of ferrocyanogen in alkaline ferrocyanides may be estimated by oxidizing to ferricyanide by means of permanganate or bichromate. With permanganate the reaction is as follows:

$$5K_4Fe(CN)_6 + KMnO_4 + 4H_2SO_4 = 5K_3Fe(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O$$

The permanganate is added until the color changes from yellow to reddish yellow. If any doubt exist as to the point, a drop may be taken out by means of a glass rod, and tested with a drop of ferric chloride. If unchanged ferrocyanide remains, it produces a blue color. If the substance to be examined contains sulphides, these must be removed by previous addition of lead carbonate, and if sulphocyanide be present, the method is altogether inapplicable.

c.c. $\frac{n}{10}$ permanganate $\times \cdot 03688 = K_4Fe(CN)_6$
" " " $\times \cdot 04228 = K_4Fe(CN)_6 + 3H_2O$

BY PRECIPITATION WITH COPPER SULPHATE.*

Applicable in presence of Sulphocyanides.

The copper solution contains 10 gms. copper sulphate ($CuSO_4 + 5H_2O$) per litre. It is added to the fluid containing a little free sulphuric acid until a drop of the turbid fluid, placed upon fine white filtering-paper near a drop of ferric chloride, no longer produces a blue line at the junction of the two liquids.

The strength of the copper sulphate solution is found by titrating against a known weight of pure ferrocyanide.

The method is only fit for technical purposes.

Most insoluble ferrocyanides may be converted into potassium ferrocyanide by boiling them with a strong solution of potassium hydrate and filtering from the metallic oxide left behind.

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* Bohlig, Polytechn. Notizblatt, 16, 81.

In a solution containing other substances capable of reducing permanganate, the ferrocyanide may be determined by precipitating with ferric chloride, washing the precipitate, decomposing with potassium hydrate, and titrating the filtered solution.

POTASSIUM FERRICYANIDE AND FERRICYANIDES.

POTASSIUM ferricyanide is best estimated by reducing it to ferrocyanide, and then estimating the ferrocyanide by potassium permanganate.

The reduction is best made in alkaline solution, by means of a solution of ferrous sulphate. This is added while the solution is heated, until the precipitate produced is black in color (Fe_3O_4), and heated for a few minutes longer. The fluid is then filtered, and the precipitate thoroughly washed, the filtrate is acidified with dilute sulphuric acid, and titrated with permanganate.

In the estimation by bichromate and permanganate, the fluid generally becomes slightly turbid towards the end of the reaction, but this does not interfere.

A quicker method is to dilute the solution to 300 c. c., allow the precipitated iron oxides to subside completely, take out 100 c. c., acidify, and titrate with permanganate. On account of the volume of precipitated oxides which is not taken into account, a small error is introduced.

c. c. $\frac{n}{10}$ perman. or bichrom. × ·03294 = $K_3Fe(CN)_6$

Most insoluble ferricyanides may be converted into the potassium salt by boiling with strong solution of potassium hydrate.

BY IODINE AND THIOSULPHATE.

When potassium iodide is added to an acid solution containing zinc ferricyanide, the ferricyanide is reduced to ferrocyanide and iodine separates.

$$2Zn_3(Fe(CN)_6)_2 + 4HCl + 4KI = 3Zn_2Fe(CN)_6 + 4KCl + H_4Fe(CN)_6 + 4I$$

The iodine is then measured by means of $\frac{n}{10}$ thiosulphate and starch. Dissolve the ferricyanide in water, add some crystals of potassium iodide free from iodate, and allow them to dissolve; then add hydrochloric acid and a sufficient amount of solution of zinc sulphate to precipitate all the ferricyanogen. Allow to stand a few minutes, add an excess of sodium bicarbonate and a few drops of starch solution, and run in $\frac{n}{10}$ thiosulphate until the blue color is destroyed.

c. c. $\frac{n}{10}$ thiosulphate × ·03296 = $K_3Fe(CN)_6$

PHOSPHORUS.

Phosphorus is always determined volumetrically as phosphoric acid.

PHOSPHORIC ACID.

EXCEPT in certain special cases where phosphoric cid must be determined rapidly, and the very reatest degree of accuracy is not necessary, phoshoric acid should be determined gravimetrically, eferably by precipitation as phospho-molybdate ammonia, if iron, alumina, etc., be present. This ecipitate is then dissolved in ammonia, and the osphoric acid precipitated as ammonium magneum phosphate, ignited, and weighed. With carel work, this method yields results which are most perfectly accurate. Detailed directions will found in works on gravimetric analysis.

BY URANIUM ACETATE.

When a solution of uranic acetate, made acid by cetic acid, is added to a solution containing phoshoric acid, the phosphoric acid is completely preipitated as uranic phosphate, $Ur_2O_3P_2O_5 + Aq$, or in resence of ammoniacal salts, $2(Ur_2O_3),NH_4OP_2O_5 +$ q.[*]

The proportion which the P_2O_5 bears to the uraium is the same in both these salts, and, for anaytical purposes, it makes no difference which is ormed.

Solutions Required.

1. A solution of uranic acetate or nitrate, made y dissolving about 34 gms. to a litre.

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[*] Sutton, Vol Anal. p. 218, Phila. 1876.

2. Solution of sodium phosphate, made by dissolving 10·0877 gms. of the pure uneffloresced crystals, which have been dried by powdering them and pressing between filter-paper, in a litre of water.

3. A solution of sodium acetate, made by dissolving 100 gms. of the salt in water, adding 100 c. c. acetic acid, sp. gr. 1·04, and diluting to a litre.

4. A solution of potassium ferrocyanide, made by dissolving a few crystals in water.

The solution of sodium phosphate is taken as the standard, and must be carefully prepared from pure materials. Sutton recommends that, as a check, 50 c. c. of the solution be measured into a platinum crucible, evaporated to dryness, ignited at a strong heat, and weighed. The sodium pyrophosphate obtained should weigh ·1874 gms.

The strength of the uranium solution is found by titrating against 50 c. c. of the sodium phosphate solution. It should be so regulated that 20 c. c. uranic solution are equal to exactly 50 c. c. of the sodium phosphate.

The analysis is made as follows: The substance to be analyzed should contain about ·1 gm. P_2O_5. It is dissolved in water, or as little acetic acid as possible, 5 c. c. of the sodium acetate solution added, and the solution diluted with water till it amounts to 50 c. c. Attention must be paid to this point, since great variations in the amount of dilution and of sodium acetate, acetic acid, and ammo- ium salts present, influence the end reaction. The tion is now heated to a temperature just below iling point, and uranium solution run in at 5 c. c., then by smaller portions at a time.

After each addition, a drop of the liquid is taken out upon a porcelain plate, and added to a drop of the ferrocyanide solution. As long as phosphoric acid remains in solution, no change occurs; but as soon as the uranium solution is in excess, a faint brownish color, due to uranic ferrocyanide, is produced. When ammonia is present, this brown color is produced sooner than when it is absent, and it is hence necessary, when we estimate phosphoric acid in a solution containing ammonia, to find the strength of the uranium solution by titrating against 50 c. c. sodium phosphate, to which 2 or 3 c. c. of a standard solution of ammonium chloride have been added.

BY FERRIC SALTS.

The method is precisely the same in principle as the one previously described, a ferric instead of a uranic salt being employed. The method by ferric salts, however, while it has the disadvantages which attend the use of the uranium method, has some additional ones peculiar to itself. The moment when the ferric salt is in excess is determined by testing with a drop of ferrocyanide, when a blue color is produced. Ferric phosphate itself, however, is colored blue by ferrocyanide, and we must hence filter the solution by some means before testing it. This is best done by taking out a drop of the solution and placing it upon a piece of filter-paper, which lies upon a second piece of the same kind. As soon as the fluid has soaked through, the upper piece is lifted off, and a drop of ferrocyanide touched to the middle of the wet spot produced on the lower piece. If a blue color is produced, the reaction is completed. This plan is better in this case than to test with the drops placed near one another upon filter-paper, and allowing them to run together. The solution of ferric salt, when it runs into the fluid containing the phosphoric acid, being changed to ferric acetate; and ferric acetate, if it be allowed to pass through several thicknesses of filter-paper, gives up a part of its iron, which remains in the paper. For this reason, it is best to make the solution travel no further through filter-paper than can be avoided. If the ferric phosphate be allowed to stand for any length of time in a solution containing an excess of ferric acetate, it alters in composition, taking iron from the solution. For this reason, it is necessary to finish the titration as rapidly as can be conveniently done, and testing the fluid for excess of iron immediately after each addition, simply stirring the fluid beforehand. As with the uranium method, the substance taken should contain about ·1 gm. P_2O_5, and the volume of liquid be about 50 c. c. A convenient substance for preparing the iron solution is ferric ammonium sulphate (Iron Alum).

By Lead Salts.

Mohr gives a method for the estimation of phosphoric acid by lead salts; the end of the reaction being the point at which a precipitate ceases to form. The method has no advantage over the two preceding.

BY PRECIPITATION AS URANIC PHOSPHATE AND ESTIMATING THE URANIUM.*

The solution containing the phosphate, which may be dissolved in water, acetic, dilute hydrochloric, or even a small quantity of nitric acid, is diluted to a definite volume, and 50 or 100 c. c. measured out for analysis. When mineral acid is present, a corresponding quantity of ammonium acetate is added, then ammonia in excess, and finally acetic acid to acid reaction. The solution is heated to boiling, and an excess of a solution of uranium acetate added. Boil for a few minutes, then allow the precipitate to settle and decant the clear liquid (which must have a clear yellow color from excess of uranium acetate) upon a filter, and wash the precipitate by decantation with a hot solution of ammonium chloride (made by adding to a saturated solution 3 or 4 volumes of water). Finally bring the precipitate upon the filter and wash thoroughly with the solution of ammonium chloride. The precipitate is dissolved in hot dilute sulphuric acid on the filter, and the filtrate and washings reduced by means of amalgamated zinc and platinum. (See under Iron.) The reduction is from Ur_2O_3 to UrO, and requires from 15 to 30 minutes for its completion. The resulting solution is poured off from the zinc and titrated with $\frac{n}{10}$ permanganate.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 00142 = P_2O_5$$

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* Belohoubek, Fres. Zeitschrift, 16, 104.

ALKALIMETRIC METHOD.*

The phosphoric acid must be precipitated as ammonia magnesium phosphate, which is accomplished as follows: The solution, which must contain neither iron, alumina, barium, strontium, lime, nor any of the heavy metals, is brought to a small volume and made alkaline by means of ammonia. Chloride of ammonium and magnesia mixture † are then added, and the solution rapidly agitated by stirring with a glass rod. The precipitation, under these circumstances, is complete in 2 or 3 hours. The precipitate is collected on a filter and washed with a mixture of 3 parts water and 1 part ammonia solution until the filtrate, when acidified with nitric acid, is no longer rendered turbid by silver nitrate. The precipitate and beaker are now further washed with spirit of wine of neutral reaction until the filtrate no longer renders red litmus paper blue, then the filter and contents are returned to the beaker, 100 to 200 c. c. water added, then a few drops of solution of cochineal and $\frac{n}{10}$ acid run in with constant stirring until the color of the cochineal changes from violet to yellow, and remains so upon standing.

The process depends upon the fact that the ammonium magnesium phosphate is alkaline to cochineal, and that this continues until the ammonia which it contains is saturated by an acid.‡

$$\text{c. c. } \tfrac{n}{10} \text{ acid} \times \cdot 00355 = P_2O_5$$

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* Stolba, Fres. Zeitschrift, 16, 100.

† Made by dissolving 1 part magnesium chloride and 1 part ammonium chloride in 8 parts water, adding 4 parts ammonia sp. gr. 0·96, allowing to stand, and filtering.

‡ See also Maly, Fres. Zeit. 15, 417.

ESTIMATION OF PHOSPHORIC ACID IN BONE ASH, ETC.

SUTTON recommends that the uranium be titrated against a solution containing a known amount of tribasic calcium phosphate. Such a solution may be made by dissolving about 4·5 gms. of the tribasic phosphate in nitric acid, and diluting to about 50 c. c., then taking a measured volume in a platinum crucible, adding ammonia, and evaporating to dryness, then igniting, gently at first to expel the ammonium nitrate, afterward more strongly, placing the crucible under the desiccator until cool, and then weighing it as rapidly as possible. After the solution is diluted to the proper strength, it must contain 2 gms. P_2O_5, or 4·3662 gms. $Ca_3P_2O_8$ per litre, and 20 c. c. of such a solution evaporated to dryness and ignited as above should give ·0873 gms. $Ca_3P_2O_8$. The uranium solution is standardized by means of this solution of calcium phosphate; 50 c. c. of the phosphate solution are measured into a beaker, and strong solution of sodium hydrate added until a cloudiness is perceptible, then 5 c. c. of the sodium acetate solution, which causes the fluid to become clear again. Nearly 20 c. c. of the uranium solution are then added at once, the solution heated nearly to boiling, and uranium added by small portions until the brown coloration is produced with potassium ferrocyanide. Where calcium phosphate is present, it is necessary to add nearly all the uranium solution at once, and without heating, since if this were not done, some of the calcium phosphate might be precipitated along with the uranic phosphate, and the accuracy of the process diminished. It will be noticed that in testing the fluid for excess of uranium when the process is finished and the uranium is in excess, the brown color caused by mixing the two drops gradually becomes more intense upon standing. For this reason, both in standardizing the uranium solution and in making the analysis, it is best to note the color produced immediately upon adding the drop of ferrocyanide without waiting. If we wait for the development of the color, the same length of time must be allowed in every case.

ESTIMATION OF PHOSPHORIC ACID IN GUANO, SUPERPHOSPHATES, ETC.*

When the guano or superphosphate contains less than ½ % iron and alumina, the phosphoric acid may be estimated by precipitation from the solution in water to which acetic acid has been added, by the standard uranium solution. If much iron or alumina be present, the best plan is to precipitate the whole of the phosphoric acid from the watery extract by adding nitric acid and ammonium molybdate. The precipitate is washed, dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture as ammonium magnesium phosphate. This is collected on a filter, and its amount determined by burning and weighing, or by titration with standard acid.

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* The proper treatment of this subject would require too much space for a volume of this size. For details, the following papers may be consulted: Fres. Zeit. 10, 133; Ibid. 16, 182. See also Sutton's Volumetric Analysis, which is very full upon this subject.

For methods of determining the "gone-back" phosphoric acid, the student must consult the works of Sutton, Fresenius, and Mohr. A great deal of quackery is prevalent as regards the methods of determining phosphoric acid in artificial manures, and statements upon the subject must be carefully examined, and their source ascertained before being accepted as true.

SULPHUR COMPOUNDS.

SULPHUR.

Sulphur is best estimated by converting it into sulphuric acid. This is easily accomplished by heating the finely-powdered substance with strong nitric acid to which some crystals of potassium chlorate have been added. The solution is covered with a watch-glass until all spirting has ceased, and then evaporated to dryness on the sand-bath with an excess of pure hydrochloric acid. The residue is dissolved in hydrochloric acid, and again evaporated to dryness, re-dissolved in water, a few drops of hydrochloric acid added, and the sulphuric acid estimated by $\frac{n}{10}$ barium chloride. (See Sulphuric Acid.) The sulphur of most insoluble sulphides may be oxidized to sulphuric acid and determined in the same way. The object of the evaporations is to drive off the nitric acid, which interferes with the estimation of the sulphuric acid.

The sulphur in sulphides may also be oxidized by fusion in a glass tube, with nine to ten times their weight of a mixture of equal parts of nitre and dry sodium carbonate.* The tube used is six inches in length, sealed at one end, and may be made from combustion tubing. In the open end, a cork and delivery-tube are inserted, the latter reaching to the bottom of the flask in which the titration is to be made. One gramme of the finely-powdered sulphide, intimately mixed with ten times as much of the nitre and sodium carbonate mixture, is introduced in this tube without loss, and the cork with the delivery-tube inserted. The end of the delivery-tube is then placed in a flask, and the tube containing the sulphide heated in small portions at a time, with the Bunsen lamp, commencing, as usual, with the anterior portion. When the operation is progressing favorably, the deflagration proceeds for a few seconds after removing the flame. There is no danger to be apprehended, and with proper care the tube does not crack or blow out. When deflagration ceases, a coil of wire gauze is slipped over the tube, and this is heated more strongly by means of a gas flame. It is not necessary that the contents be perfectly fused. The gaseous products of the combustion carry over sulphates which collect in the bottom of the flask. They are brought into solution by adding some water, covering the mouth of the flask with the palm of the hand, and shaking. The delivery-tube is rinsed into the same flask, and the ignition-tube, with its contents broken, placed in the flask, and hydrochloric acid added to bring the contents in solution. The solution is nearly neutralized with ammonia, and the sulphuric acid determined by $\frac{n}{10}$ barium chloride.

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* Holland, Chem. News, xxvii. 15.

ALKALIMETRIC METHOD FOR SULPHUR IN SULPHIDES.

This method is best adapted for the estimation of sulphur in copper and iron pyrites for technical purposes. The results are by no means exact, and vary at times as much as 1½ %.

One gm. of the very finely-powdered sulphide is mixed intimately with 5 gms. pure dry sodium carbonate; 5 gms. potassium chlorate and 5 gms. decrepitated sodium chloride are then added, and the whole mixed together in a platinum, iron, or copper crucible. The mixture is then heated to dull redness for 10 minutes. The sulphide is oxidized, and the sulphuric acid formed combines with a portion of the sodium carbonate, expelling an equivalent amount of carbonic acid.

The mass is cooled, dissolved in water, the solution made up to 500 c. c., 100 c. c. taken out with a pipette, and the amount of sodium carbonate remaining determined by normal acid.

A better plan is to filter the solution, wash the residue well, and estimate the sodium carbonate in excess by normal acid as above. The inaccuracy of the process is caused by the volatilization of some of the sulphur in the form of chloride, and also the formation of ferric sulphate from which the acid is expelled at a red heat. The reaction involved is as follows:

$$2FeS_2 + 5KClO_3 + 4Na_2CO_3 = Fe_2O_3 + 4Na_2SO_4 + 5KCl + 4CO_2$$

The sodium chloride is used to moderate the violence of the reaction. Where roasted pyrites is under examination, it may be entirely dispensed with.

$$Na_2CO_3 \times \cdot 3016 = S$$

Kolb's modification of the above process.—If the ore contains more than 10 % sulphur, 5 gms., if less, 10 gms. of the finely-powdered substance is intimately mixed with 50 gms. finely-pulverized cupric oxide, and 5 gms. pure dry sodium carbonate. The mixture is heated in a dish of platinum, iron, or copper, but not to full redness. After about 15 minutes' heating, the mass is cooled, dissolved in water, and the excess of sodium carbonate estimated in the filtered solution. This process is especially adapted to the technical examination of roasted pyrites.

ESTIMATION OF SULPHUR IN ALKALINE SULPHIDES.

The estimation is the exact reverse of the process for estimating zinc by sodium sulphide. The zinc solution is made by dissolving 22·1717 gms. zinc potassium sulphate ($ZnSO_4.K_2SO_4,6H_2O$) in water, adding ammonia until the zinc hydrate at first precipitated is redissolved, and diluting to a litre.

The zinc potassium sulphate is made by mixing hot solutions of zinc and potassium sulphates in the proportion of 287·16 $ZnSO_4 \cdot 7H_2O$ to 174·274 K_2SO_4, and allowing the solution to cool while it is constantly stirred. The crystals are dried with the Bunsen pump and by pressure between filtering-paper.

If perfectly pure zinc can be obtained, 3·258 gms. dissolved in hydrochloric acid, and after addition of sufficient ammonia diluted to a litre, gives a solution of the same strength. The sulphide is dissolved in water, and the zinc solution added until a drop taken out and tested on filter-paper, with the alkaline lead solution, no longer gives the black ring at the point of contact. As in the estimation of zinc, an excess of sulphide is present as long as the black ring is formed, and when this is no longer the case, sulphide may still be present in small quantity. A correction must be applied in the same way as in the estimation of zinc, except that in the case of zinc, the correction is subtracted from the whole amount of c. c. used, while in this instance it must be added.

The following examples show about the amount of the correction necessary, and the influence of dilution. Sodium sulphide was added to pure water until the black ring made its appearance on testing with alkaline lead solution.

50 c. c. of water required ·3 c. c. Na_2S
100 " " " " ·4 " "
150 " " " " ·5 " "
200 " " " " ·65 " "

Example: ·2 gms. of a specimen of crude sodium sulphide requires 30 c. c. zinc solution. After the estimation, we measure the fluid, and find its volume to be about 70 c. c. ; 70 c. c. of water are then taken, and sodium sulphide solution, about equal in strength to the zinc solution, added drop by drop until a drop taken out gives the black ring with alkaline lead solution ; ·3 c. c. are required ; 30 c. c. − ·3 c. c. = 29·7 c. c., which, multiplied by ·0016, the equivalent of 1 c. c. in sulphur = ·04752 S = 23·76 %.

c. c. zinc solution × ·0016 = S
" " " × ·0039 = Na_2S
" " " × ·00551 = K_2S
" " " × ·0034 = $(NH_4)_2S$

Sulphides may also be estimated by adding an excess of zinc solution, washing the precipitated sulphide rapidly out of contact of air, digesting with an excess of ferric sulphate, and estimating the ferrous salt with permanganate (see Zinc) ; $\frac{n}{10}$ permanganate × ·0016 = S.

Sulphydric acid may be measured by either of these methods, but not with very great accuracy.

SULPHYDRIC ACID.

By Permanganate.

When ferric sulphate is added to a solution of H_2S in water, the following reaction takes place :

$$Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S$$

The sulphur separates as a white powder, making the fluid milky. The $FeSO_4$ formed is a measure of the H_2S, and may be estimated by permanganate. The finely-divided sulphur does not interfere.

An acid solution of ferric sulphate, which must of course be free from ferrous sulphate, is poured into a flask, and the solution of hydrogen sulphide measured in from a pipette whose point just touches the surface of the solution in the flask. The flask is closed and allowed to stand for an hour, shaking occasionally. At the end of this time, the fluid must still possess a yellowish color, due to excess of ferric sulphate, and upon opening the flask, no smell of hydrogen sulphide should be noticed. The solution is diluted and titrated with permanganate. If the solution of hydrogen sulphide is very dilute, it should stand 3 or 4 hours before being titrated.

When the solution containing H_2S also contains thiosulphates, or other substances which exercise a reducing action upon permanganate, the H_2S must be precipitated by ammoniacal zinc solution added in excess, the precipitate rapidly washed, transferred to a flask containing an acid solution of ferric sulphate, and after standing half an hour in a warm place, the solution diluted and titrated by permanganate.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 0017 = H_2S$$

BY IODINE AND THIOSULPHATE.

When iodine and hydrogen sulphide are brought together in solution, the following reaction occurs:

$$H_2S + 2I = 2HI + S.$$

The reaction is not regular, however, when performed in acid solution. Mohr has found that when ammonium carbonate or bicarbonates of the alkaline metals are added to the solution to alkaline reaction, the results are constant and represented by the above equation.

The solution of H_2S is diluted, carbonate of ammonia added until the solution reacts alkaline to litmus paper, starch added, and then iodine solution until the blue color appears. Where great exactness is required, it is preferable to add starch to a quantity of water, and color light blue by a drop or two of iodine, then add the solution of H_2S and some ammonium carbonate, and then run in iodine until the same color is produced.

$$\text{c. c. } \tfrac{n}{10} \text{ iodine} \times \cdot 0017 = H_2S$$

The estimation may likewise be made by adding the solution of H_2S to a solution of copper sulphate, boiling for a few minutes, filtering off the precipitated sulphide, dissolving it in nitric acid, evaporating the solution to dryness, with excess of sulphuric acid, and estimating the copper by means of potassium iodide and sodium thiosulphate. (See Copper.)

$$\text{c. c. } \tfrac{n}{10} \text{ thiosulphate} \times \cdot 0017 = H_2S$$

BY SODIUM ARSENITE.

When H_2S is added to a solution of sodium arsenite, the reaction which occurs is as follows:

$$Na_2As_2O_4 + 3H_2S = 2NaOH + As_2S_3 + 2H_2O$$

Add the solution of H_2S to a solution of sodium arsenite, acidify slightly by means of hydrochloric acid, filter off the precipitated arsenious sulphide, add ammonium carbonate to the filtrate to alkaline reaction, and measure the excess of arsenious acid by $\frac{n}{10}$ iodine and starch.

$$\text{c. c. } \tfrac{n}{10} \text{ sodium arsenite} \times \cdot 00255 = H_2S$$

BY SILVER NITRATE AND SODIUM CHLORIDE.

The solution of hydrogen sulphide is added to an excess of $\frac{n}{10}$ silver nitrate (see Silver), and the precipitate of Ag_2S filtered and washed. In the filtrate, the excess of silver is determined by one of the methods given under Silver. If it be estimated by means of sodium chloride with chromate as indicator, it is necessary to first neutralize the free acid produced by the action of the hydrogen sulphide upon the silver nitrate by means of a weak solution of sodium carbonate.

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3$$

$$\text{c. c. } \tfrac{n}{10} \text{ silver solution} \times \cdot 0017 = H_2S$$

ESTIMATION OF SULPHUR AND AMMONIA IN ILLUMINATING GAS.

SADLER and Silliman, in a paper read before the American Institute of Mining Engineers, and published in the *American Chemist*, vol. vii. p. 349, have described a volumetric process for estimating sulphur and ammonia in illuminating gas, which has advantages over the gravimetric process. The following description is taken from their paper.

Description of the Apparatus.

The apparatus represented in Fig. 40* is of glass, except the governor *b*, the meter *i* with its connections, and the burner with its case *k*, which are of metal; *d* performs the office of a scrubber. It is an inverted calcium chloride or bubbling tube of about 600 c. c. capacity, with a third hole drilled for the admission of the stopper *h*, which carries a wire to support ammonia, acid, and hydrogen sulphide test-papers. The larger cylinder is filled with broken glass and supplied with standardized acid from the bottle *u* by means of the syphon tube *g*, which is fitted with a stop-cock. The gas is admitted by the tube *c*, extending 5 cms. into the cylinder, and the acid escapes into a flask* below by the tube *e*, which is bent to form a seal. The meter and burner are substantially those used by the Referees.† The adaptor or eductor *l* is 50 to 60 c. c. high, the diameter at the base about 7 cms., and the smallest internal diameter at least 1½ cms.; *m* has a diameter of 2 cms., with an opening drawn out at the bottom for the escape of the drip from

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* By an error of the engraver, a beaker was substituted for a flask in the cut.

† First report of the Gas Referees upon the sulphur question, July 13th, 1870. Reported in London *Journal of Gas-Lighting*, etc., August 16th, 1870.

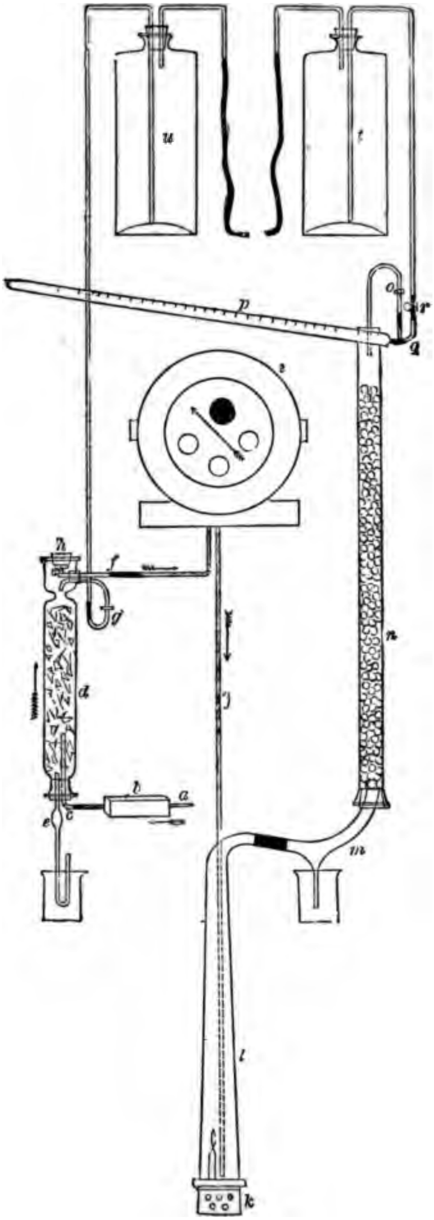

FIG. 40*.

n; *n* is a strong tube 3½ cms. in diameter by 80 cms. long, filled with glass marbles 1½ cms. in diameter. This tube serves as a condenser, and also to break up the ascending current from the burner, and bring it into intimate contact with a standard alkali, dripping upon the marbles through the tube and stop-cock *o*, from the pipette *p*. This measures 200 c. c. by halves, and is 60 cms. long. At the beginning of an experiment, it is filled by the three-way pipe *q* from the bottle *t*, by opening the pinch-cock *r*.

The apparatus is most conveniently mounted against the wall; the meter and bottles standing upon shelves, and the burner and flasks upon swinging brackets. The remaining parts are then secured by clamps driven or screwed into the wall.

Mode of Manipulation.

Solutions of caustic soda or potash and an acid, sulphuric or oxalic, are provided, of such strength that 1 c. c. has a saturating power exactly equal to $\frac{1}{10}$ grain of sulphur in the form of sulphurous or sulphuric acid. The containing bottles and the pipette being filled, the gas is lighted and regulated by the governor, as near as may be to the rate of ten feet in twenty-four hours. The stop-cocks in *o* and *g* are then opened so that 10 c. c. will pass each for one foot of gas burned.* After half an hour or an hour, when the apparatus has attained its normal working, a clean flask is placed under each drip, while the meter and the quantity of alkali solution in the pipette are accurately noted.

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* Great difficulty was experienced in securing an uninterrupted and uniform flow of the solutions. The purest distilled water seemed to carry down impurities sufficient to choke the capillary openings of the stop-cocks, which, at the proper rate, pass but four drops per

When, thereafter, 10 feet have passed the meter, which will be in about twenty-four hours, the quantity of alkali which has flowed from the pipette is determined and the flasks are removed, others being substituted if a test is desired for the following day.

The free and carbonated alkali present in the drip is then to be saturated with the standard acid; but since with litmus, and even with cochineal,* the carbon dioxide obscures the point of neutralization, it is best to add a quantity of acid equal to the total alkali used, and, after removing the carbon dioxide by boiling the liquid for a brief interval, to titrate back with the standard alkali. The number of c. c. so used expresses the number of grains of sulphur in 100 feet of gas. For the alkali

minute. Filters of Swedish paper, of cotton batting, of fine linen cloth, and of sand, were tried in vain. The simple device of passing the solutions through the stop-cocks in ascending, instead of descending currents, which placed the force of gravity in opposition to, instead of in accord with, the slow suction of the streams, afforded instant and complete relief.

* Hæmatoxylin was first chosen as an indicator, both because it is the most sensitive to minute quantities of free acid and alkali, and because the change of color, yellow to port wine, is the most conspicuous. But in this solution the reaction was very unsatisfactory. The color changed gradually from yellow to reddish brown. The absence of metallic salts, at least of the heavy metals, was well demonstrated, and there seemed no explanation of the phenomenon, except that the coloring matter was oxidized by the nitrous acid present, and rapidly destroyed. Cochineal was therefore substituted, and proved very satisfactory.

received in the drip being just saturated by the standard acid, the free acid there will be the quantity caught by the gas. Now, since 1 c. c. of the alkali finally added is saturated by one tenth grain of sulphur, one tenth of the c. c. added indicates the number of grains caught from the 10 feet burned, and ten times this the quantity of sulphur in 100 feet.

The acid solution used in the scrubber is also measured, and the acid remaining free determined by the standard alkali. The difference expresses (as in the case of the sulphur test) the number of grains of sulphur which can be neutralized by the ammonia in 100 feet of gas. Since one grain of sulphur neutralizes $1\frac{1}{16}$ grains of ammonia, if the number of c. c. of acid neutralized by the ammonia be increased by $\frac{1}{16}$, the sum will express the grains of ammonia in 100 feet. This may be accomplished mechanically by having the ammonia measuring glasses graduated so that 17 divisions shall be equal to 16 c. c. The conditions indicated are the most convenient for continuous daily determinations. They are not essential to successful working. On the contrary, two feet of gas are sufficient to give reasonably accurate results, and the apparatus has not proved unequal to a rate of one foot per hour. Moreover, much less acid run through the scrubber would be usually sufficient. For further details concerning the sources of error incident to the process, etc., the student is referred to the original paper.

Upon the estimation of sulphur in illuminating gas, see also Brügelmann, Fres. Zeitschrift, 15, 175, and 16, 24.

An excellent method for estimating sulphur in organic compounds, described by Weidel and Schmidt, consists in burning the substance in a hard glass tube, in a current of oxygen, the oxidation being completed by passing the gases over platinized asbestos. For details, the original paper may be consulted. (See Berichte der Deut. Chem. Ges. 10, 1131.)

SULPHUROUS ACID.

By Iodine.

When iodine is added to a solution of sulphurous acid previously made alkaline by ammonium carbonate or sodium bicarbonate, hydriodic and sulphuric acids are produced.

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI$$

The same reaction takes place if the solution be very dilute, containing not more than ·05 % sulphur dioxide.

The solution containing sulphurous acid is diluted with cold boiled water, and ammonium carbonate added until the solution turns red litmus paper blue. Starch solution is then added, and $\frac{n}{10}$ iodine run in until the blue color appears.

c. c. $\frac{n}{10}$ iodine × ·0032 = SO_2
"   "   "   × ·0041 = H_2SO_3

SULPHURIC ACID.

TABLE.

Specific gravity of dilute Sulphuric Acid. Temp. 15° (*Bineau*).*

H_2SO_4 per cent.	Specific Gravity.	H_2SO_4 per cent.	Specific Gravity.	H_2SO_4 per cent.	Specific Gravity.
100	1·8426	66	1·5680	33	1·2476
99	1·8420	65	1·5570	32	1·2390
98	1·8406	64	1·5450	31	1·2310
97	1·8400	63	1·5340	30	1·2230
96	1·8384	62	1·5230	29	1·2150
95	1·8376	61	1·5120	28	1·2066
94	1·8356	60	1·5010	27	1·1980
93	1·8340	59	1·4900	26	1·1900
92	1·8310	58	1·4800	25	1·1820
91	1·8270	57	1·4690	24	1·1740
90	1·8220	56	1·4586	23	1·1670
89	1·8160	55	1·4480	22	1·1590
88	1·8090	54	1·4380	21	1·1516
87	1·8020	53	1·4280	20	1·1440
86	1·7940	52	1·4180	19	1·1360
85	1·7860	51	1·4080	18	1·1290
84	1·7770	50	1·3980	17	1·1210
83	1·7670	49	1·3886	16	1·1136
82	1·7560	48	1·3790	15	1·1060
81	1·7450	47	1·3700	14	1·0980
80	1·7340	46	1·3610	13	1·0910
79	1·7220	45	1·3510	12	1·0830
78	1·7100	44	1·3420	11	1·0756
77	1·6980	43	1·3330	10	1·0680
76	1·6860	42	1·3240	9	1·0610
75	1·6750	41	1·3150	8	1·0536
74	1·6630	40	1·3060	7	1·0464
73	1·6510	39	1·2976	6	1·0390
72	1·6390	38	1·2890	5	1·0320
71	1·6370	37	1·2810	4	1·0256
70	1·6150	36	1·2720	3	1·0190
69	1·6040	35	1·2640	2	1·0130
68	1·5920	34	1·2560	1	1·0064
67	1·5800				

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* See also Kolb, Fres. Zeit. 12, 333.

BY SATURATION.

The free acid may be estimated by adding litmus and normal alkali until the color changes.

$$\text{c. c. normal alkali} \times \cdot 0040 = SO_3$$
$$\text{" \quad " \quad "} \times \cdot 0049 = H_2SO_4$$

In solutions containing free sulphuric acid and sulphates of the heavy metals, the free acid is estimated with Kieffer's ammoniacal copper solution (see page 68).

ESTIMATION OF SULPHURIC ACID IN SULPHATES ALKALIMETRICALLY.

By Barium Chloride (*Carl Mohr*).

The sulphuric acid is precipitated from the solution slightly acidified with hydrochloric acid by means of an excess of a solution of barium chloride, containing 121·9579 ms. pure barium chloride ($BaCl_2 + 2H_2O$) per litre. The solution is heated to boiling for a few minutes, and the excess of barium precipitated with ammonium carbonate in slight excess. Wash the mixed precipitate of sulphate and carbonate until the filtrate ceases to turn red litmus blue, dissolve the carbonate in a slight excess of normal acid, and estimate the excess by normal alkali. From the data so obtained, it is easy to find how much of the barium chloride added was necessary for the precipitation of the sulphates.

c. c. normal barium chloride × ·0040 = SO_3
" " " " × ·0049 = H_2SO_4

The method is inapplicable in presence of acids which precipitate barium from alkaline solution. If much free acid be present, it must be nearly neutralized with sodium carbonate.

*By Barium Hydrate.**

To the aqueous solution of the substance, a slight excess of baryta-water is added, and then seltzer water, which precipitates the excess of baryta. The liquid is separated by decantation, boiled, and filtered with the first precipitate. The precipitate having been washed, the filtrate is colored with litmus, and neutralized with a standard solution of sulphuric acid. The amount of acid necessary is of course exactly equal to that which was originally combined with the alkalies. This method is of great advantage where sulphates of lime, magnesia, etc., are present.

By Lead Nitrate.

The sulphuric acid is precipitated in neutral or only very slightly acid solution by means of lead nitrate, the precipitated lead sulphate washed by means of water which has previously been saturated with lead sulphate by agitation with some of it. The lead sulphate is washed from the filter into a beaker, and some ammonium carbonate and ammonia added.

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* Jean, Compt. Rend., lxxxiii. 973; J. Chem. Soc. vol. 1, 1877, p. 738.

The solution is heated gently, when the lead sulphate is completely converted into carbonate. This is then brought upon the same filter, washed thoroughly with hot water, dissolved in a measured quantity of normal nitric acid, and the excess of acid found by normal sodium carbonate. (See Lead.) Mohr obtained in the analysis of potassium sulphate by this method, 100·11 and 99, instead of 100 %.

Direct Method by Strontium Chloride.

The method is like the above in principle. Strontium chloride is added in slight excess, and then half the volume of alcohol, and the mixture allowed to stand 12 hours. The solution is then filtered, washed with a standard solution of strontium sulphate, and the strontium sulphate decomposed by ammonium carbonate and hydrate, washed, dissolved in an excess of normal acid, boiled to expel CO_2, litmus added, and then normal alkali until the color changes to blue.

Mohr obtained 99 and 99·5 instead of 100 % in the estimation of pure K_2SO_4 by this method.

By Precipitation with $BaCl_2$ in Excess, and Estimating the Excess with Potassium Chromate.[*]

The solutions required are:

Solution of barium chloride, which is preferably made of decinormal strength, or 12·1957 gms. barium chloride ($BaCl_2, 2H_2O$) per litre.

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[*] Wildenstein, Fres. Zeit. 1, 323.

Solution potassium bichromate, also decinormal, and containing 7·3808 gms. of the salt per litre.

The solution must be neutral or very slightly alkaline, and contain no carbonic or other acid, besides sulphuric, capable of precipitating barium from a neutral solution. If the solution contains carbonates, a slight excess of pure hydrochloric acid is added, and the solution boiled until all carbon dioxide is driven off, and then ammonia free from carbonate added to alkaline reaction. The solution is heated to boiling, and then barium chloride added in excess. Ammonia free from carbonate is added, and then potassium bichromate by small portions, boiling after each addition, until the fluid remaining above the precipitate, which subsides rapidly, is of a faint yellow color.

The c. c. barium chloride used − c. c. bichromate = c. c. barium necessary, which × ·0040 = SO_3 × ·0049 = H_2SO_4.

Precipitation in Acid Solution by Standard Barium Chloride (*Wildenstein*).

Wildenstein first proposed this method of estimating sulphuric acid in acid solution, which is almost universally applicable, since, with the exception of barium sulphate, all barium salts are soluble in dilute hydrochloric acid. The end of the reaction, according to Wildenstein, is the point when further addition of barium chloride ceases to produce a precipitate. Barium sulphate is deposited rapidly from a hot solution containing excess of sulphuric acid, leaving a clear solution, but as the excess of acid grows smaller, it settles more slowly until, near and beyond the neutral point, we must either wait a long time for the precipitate to settle, or by some means filter a small portion of the fluid, and test the filtrate to see whether enough barium chloride has been added. For the filtration, Wildenstein employs the following special apparatus, shown in Fig. 41. A is a bottle of white glass whose bottom has been removed, and which will contain about 900 c. c. An ordinary quart bottle answers the purpose. The bent funnel-tube B is covered in the following way: A piece of muslin is first laid over the aperture, then two pieces of fine Swedish filter-paper, and finally another piece of muslin. The whole is then fastened tightly over the mouth of the tube by means of waxed thread, and the projecting edges neatly trimmed. In binding over the aperture, care must be taken not to break the filter-paper. Fill the vessel with hot water above the funnel-tube, and by opening the pinch-cock, the funnel-tube is completely filled. Add the solution of the sulphate, which is to be estimated, and acidify with a few drops of hydrochloric acid, and then add the barium chloride from the burette gradually, after each addition opening the pinch-cock and allowing a volume of fluid corresponding to the contents of the tube to flow into a small beaker; this is then returned to the beaker, another portion run out into the same beaker without rinsing it, and this tested by a drop of barium chloride from the burette. If a precipi-

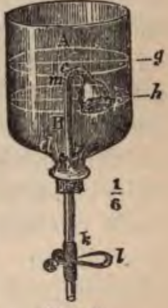

FIG. 41.

tate forms, the contents of the beaker are returned to the bottle, a little more barium chloride added, the contents of the tube emptied and returned to the beaker, and then a second portion run into the beaker and tested, and so on until the solution fails to give a perceptible precipitate with a drop of barium chloride after the lapse of two minutes. It is necessary to empty the contents of the tube each time before testing, since the barium chloride which is added to the solution in the bottle does not enter the funnel-tube until the pinch-cock is opened. Care must be taken not to injure the filter in stirring the fluid. If the point is overstepped, one or two c. c. of a solution of sulphuric acid, corresponding in strength to the barium solution, may be added, and the titration then completed with barium solution. In the precipitation of sulphuric acid by barium chloride, a point occurs, as in the silver assay, where both barium chloride and sulphuric acid produce a precipitate. This point marks the time when barium chloride and sulphuric acid are present in solution in precisely equivalent quantities; and if this point be taken as the end of an analysis, we need only weigh out 12·1957 gms. pure $BaCl_2 + 2H_2O$ to a litre of water, and use this fluid without any further testing. If, however, we proceed as Wildenstein recommends, rather more than an equivalent of barium chloride is required for each equivalent of sulphuric acid, and we must measure the "working strength" of the solution by titrating against a weighed amount of some sulphate, and for this purpose, copper sulphate, $CuSO_4 + 5H_2O$, answers very well, and is easy to procure perfectly pure.

Brügelmann* describes a modification of Wildenstein's apparatus, which has the advantage that precipitation can be conducted in ordinary beakers. The liquid to be titrated is contained in a beaker, and is heated over a gas flame to the temperature most favorable to the rapid precipitation of barium sulphate. The apparatus for removing filtered samples of liquid from the beaker consists of a small funnel containing filter-paper and cotton-wool, and hanging in the liquid; this is joined to a longer tube outside, so as to form a syphon by means of a piece of India-rubber tubing, which forms the bend of the syphon. This syphon-filter is filled with hot water, its longer limb closed by a piece of India-rubber tubing and pinch-clamp, and the funnel suspended in the liquid in the beaker. The arrangement proved very useful, and yielded very accurate results in determinations of sulphur in animal and vegetable substances, and in coal-gas.

Instead of Wildenstein's apparatus or that of Brügelmann, the filtering pipette may be used. Instead of finding the point where barium chloride ceases to produce a precipitate, it is better to find the point where both barium chloride and sulphuric acid produce precipitates in portions of the clear solution. After a little practice, it is easy to hit this point, and the barium solution can then be made by simply weighing out 12·1957 gms. pure barium chloride and dissolving in a litre, the strength of a corresponding solution of sulphuric acid being found by titration against the barium chloride. The solutions may then be also used for estimating barium, for which they would not be so well adapted if Wildenstein's method were taken.

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* Zeit. Anal. Chem. xvi. 19; J. Chem. Soc. vol. 1, 1877, p. 737.

The solution containing sulphuric acid is dissolved in water in a beaker, and a few drops of hydrochloric acid added. Two burettes are then taken, one containing decinormal barium chloride, and the other sulphuric acid of equal strength. Barium chloride is run into the solution until it ceases to give a precipitate, and then sulphuric acid, then barium chloride again if necessary, adding the solutions alternately until a portion of the liquid, filtered into two small test-tubes, gives the same volume of precipitate, the one having a drop of the sulphuric acid, the other of barium chloride, added to it. c. c. $BaCl_2$ – c. c. H_2SO_3 = $BaCl_2$ necessary. The following examples show the accuracy of which the method is capable :

Copper Sulphate ($CuSO_4 + 5H_2O$) Theoretical % SO_3 = 32·08.

$$\left.\begin{array}{l} \text{No. } 1 - 31{\cdot}90 \\ \text{``}\ \ 2 - 31{\cdot}86 \\ \text{``}\ \ 3 - 31{\cdot}80 \\ \text{``}\ \ 4 - 32{\cdot}05 \end{array}\right\}\text{ Average, } 31{\cdot}92\ \%$$

Magnesium Sulphate ($MgSO_4 + 7H_2O$) Theoretical % SO_3 = 32·52.

$$\left.\begin{array}{ll} \text{Neutral solution} & \left\{\begin{array}{l} \text{No. } 1 - 32{\cdot}64 \\ \text{``}\ \ 2 - 32{\cdot}68 \end{array}\right. \\ \text{Acid solution} & \left\{\begin{array}{l} \text{No. } 3 - 32{\cdot}35 \\ \text{``}\ \ 4 - 32{\cdot}28 \end{array}\right. \end{array}\right\}\ 32{\cdot}49\text{ Average.}$$

c. c. $\frac{n}{10}$ barium chloride × ·0040 = SO_3

" " " " × ·0049 = H_2SO_4

CARBON BISULPHIDE.

BY COPPER SULPHATE.*

THE method is based upon the reaction between copper salts and xanthates, previously employed by Vogel for the detection of carbon bisulphide in coal-gas. A saturated solution of potassium hydrate in alcohol is prepared, and into this solution the carbon bisulphide is dropped and heated to boiling, when it is completely converted into potassium xanthate. The excess of caustic alkali is converted into carbonate by adding sodium bicarbonate. To this solution a decinormal solution of copper sulphate is added, until a precipitate is no longer produced. The copper xanthate settles well after agitation, so that the end of the reaction is easily recognized.

The copper solution is made by dissolving 3·168 gms. of copper, in the form of sulphate, in water, adding Rochelle salt and sodium carbonate until the precipitate at first thrown down redissolves, and diluting the solution to a litre.

$$\text{c. c. } \tfrac{n}{10} \text{ copper sulphate} \times \cdot 0076 = CS_2$$

SODIUM THIOSULPHATE AND THIOSULPHATES.

THIS is determined in neutral solution or in a solution made slightly alkaline by means of ammonium carbonate or sodium bicarbonate. Starch is added, and then $\frac{n}{10}$ iodine, until the blue color appears.

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* Grete, Berichte der Deut. Chem. Ges. ix. 921.

If the solution also contains sulphides, these are precipitated by solution of zinc sulphate, the precipitate washed, and the thiosulphate determined in the filtrate, as above.

CARBON COMPOUNDS.

CARBONIC ACID.

Carbonic acid in solution in water may be measured by adding an excess of standard baryta-water, and estimating the excess by $\frac{n}{10}$ oxalic acid. The whole of the carbonic acid is precipitated as carbonate immediately upon addition of the baryta-water, and the excess is found by adding $\frac{n}{10}$ oxalic or hydrochloric acid, until a glass rod dipped in the fluid no longer produces a brown red spot upon turmeric paper. The end of the reaction is very sharply shown (see page 41). When carbon dioxide is contained in a gaseous mixture, it may be estimated by passing through a measured volume of standard baryta-water, and, without filtering, estimating the excess of baryta. In alkaline carbonates containing bicarbonate, the excess of carbonic acid over that necessary to form neutral carbonate may be found by adding barium chloride in excess to the somewhat dilute solution, then standard baryta-water in excess, and estimating the excess by $\frac{n}{10}$ oxalic acid, as above. In this case, all the carbonic acid contained as neutral carbonate is precipitated by the barium chloride first added, but the remainder stays in solution, and is estimated by addition of the baryta-water.

$$\text{c. c. } \tfrac{n}{10} \text{ acid} \times \cdot 0022 = CO_2$$

IN SOLUBLE CARBONATES.

Carbonic acid in alkaline carbonates and bicarbonates may be estimated by adding to the hot solution barium or calcium chloride in excess. When bicarbonates are to be estimated, ammonia, free from carbonic acid, must first be added. The solution is boiled for a minute or two, filtered, and the precipitate rapidly washed with hot water. The precipitate, together with the filter, is placed in the flask in which the precipitation was made, and an excess of normal acid added, and boiled until the barium or calcium carbonate has dissolved, and the carbonic acid been driven off. Litmus is then added, and lastly, normal alkali from a burette, until the color of the litmus changes.

$$\text{c. c. normal acid} \times \cdot 0220 = CO_2$$

The barium carbonate may also be dissolved in hydrochloric acid, evaporated to hard dryness, and the amount of chlorine in the barium chloride found by $\frac{n}{10}$ silver nitrate. (See Barium.)

$$\text{c. c. } \tfrac{n}{10} \text{ silver solution} \times \cdot 0022 = CO_2$$

Either barium or calcium chloride may be used for precipitating carbonic acid from its solutions.

Calcium chloride is preferable where it can be used as calcium carbonate, is more granular and easier to wash than barium carbonate. In presence of caustic alkalies, however, barium chloride must be used, as calcium hydrate is very insoluble.

IN INSOLUBLE CARBONATES.

Carbonates insoluble in water must be decomposed with acid, and the carbonic acid received in strong ammonia, which absorbs it completely, and is afterward precipitated by calcium chloride and estimated as in soluble carbonates.

The ammonia used must be pure and free from carbonic acid. If any be present, a little calcium chloride is added, and the solution, after standing for some time in a closely stoppered bottle until the precipitate settles, is decanted and kept in the bottle, Fig. 24.

The decomposition is effected in the apparatus, Fig. 36. *A* contains the carbonate and water; *b*, hydrochloric acid; *B*, ammonia free from carbonic acid; and *c*, pieces of broken glass through which the ammonia has been poured into the flask.

To effect the transfer of the carbonic acid from the carbonate to the ammonia, the flask containing the latter is heated, causing some of it to volatilize, and filling the flask with the fumes. Acid is then run upon the carbonate from the pipette by opening the pinch-cock, and, after the decomposition of the latter is complete, the liquid is boiled, and a slow current of air free from CO_2 drawn through the apparatus to carry over the last traces of the gas.

The apparatus is disconnected, *c* is rinsed into *B*, calcium chloride is added, and the solution boiled for some time. The calcium carbonate is then filtered and washed with hot water, dissolved in the flask with normal acid in excess, and the excess found by normal alkali.

OXALIC ACID AND OXALATES.

FREE oxalic acid may be measured by direct titration either with normal alkali or by Pettenkofer's method.

c. c. normal alkali × $\cdot 063 = C_2H_2O_4 + 2H_2O$
" " " × $\cdot 036 = C_2O_3$

Oxalic acid may likewise be determined by adding an excess of calcium acetate to the solution, which must be neutral or made slightly acid with acetic acid, and free from alumina sesquioxide of chromium, copper, and ferric salts. The precipitation is made in a hot solution. The precipitate of calcium oxalate is washed with hot water, heated to redness in a crucible, whereby it is converted into a mixture of calcium carbonate and oxide, and is then dissolved in an excess of normal acid, litmus added, and the excess found by normal alkali.

c. c. normal acid × $\cdot 063 = C_2H_2O_4 + 2H_2O$
" " " × $\cdot 036 = C_2O_3$

ESTIMATION BY PERMANGANATE.

Potassium permanganate, added to an acid solution of oxalic acid, converts it into carbon dioxide and water.

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

This method of estimating oxalic acid was explained in connection with the determination of the strength of solutions of potassium permanganate (see page 48).

The oxalic acid or oxalate is dissolved in dilute sulphuric acid, heated to 30° or 40°, and the permanganate run in from a burette. The solution becomes dark brown at first, then gradually turns to yellow, and finally clear white again. The permanganate must be added slowly, and the solution shaken constantly. The solution should be allowed time to become colorless after each addition of permanganate, before more is run in. As soon as a drop of permanganate colors the liquid permanently, the reaction is completed. In absence of other substances which act upon permanganate, the results are excellent.

c. c. $\frac{n}{10}$ permanganate $\times \cdot 0063 = C_2H_2O_4 + 2H_2O$
" " " $\times \cdot 0036 = C_2O_3$

ACETIC ACID.

ACETIC acid may be determined by taking the specific gravity and comparing it with the following table.

The acid is anomalous in regard to its specific gravity after dilution, as will be seen at a glance, since this rises until the acid contains 80 %, and then decreases. For this reason, the method cannot be used for solutions containing over 40 % of the acid. Suppose, for example, we found a sample of acetic acid to possess a sp. gr. of 1·070. By comparing with the table, we find that acid of 1·0707 sp. gr. contains 64 %, and acid of 1·0705 sp. gr. 91 %, and we would be unable to tell which percentage our sample contained.

TABLE.

Specific gravity of solutions of Acetic Acid. Temp. 15°.

$C_2H_4O_2$ per cent.	Specific Gravity.	$C_2H_4O_2$ per cent.	Specific Gravity.	$C_2H_4O_2$ per cent.	Specific Gravity.
0	1·0000	15	1·0214	30	1·0412
1	1·0007	16	1·0228	31	1·0424
2	1·0022	17	1·0242	32	1·0436
3	1·0037	18	1·0256	33	1·0447
4	1·0052	19	1·0270	34	1·0459
5	1·0067	20	1·0284	35	1·0470
6	1·0083	21	1·0298	36	1·0481
7	1·0098	22	1·0311	37	1·0492
8	1·0113	23	1·0324	38	1·0502
9	1·0127	24	1·0337	39	1·0513
10	1·0142	25	1·0350	40	1·0523
11	1·0157	26	1·0363	41	1·0533
12	1·0171	27	1·0375	42	1·0543
13	1·0185	28	1·0388	43	1·0552
14	1·0201	29	1·0400	44	1·0562

TABLE—(*Continued*).

$C_2H_4O_2$ per cent.	Specific Gravity.	$C_2H_4O_2$ per cent.	Specific Gravity.	$C_2H_4O_2$ per cent.	Specific Gravity.
45	1·0571	64	1·0707	83	1·0744
46	1·0580	65	1·0712	84	1·0742
47	1·0589	66	1·0717	85	1·0739
48	1·0598	67	1·0721	86	1·0736
49	1·0607	68	1·0725	87	1·0731
50	1·0615	69	1·0729	88	1·0726
51	1·0623	70	1·0733	89	1·0720
52	1·0631	71	1·0737	90	1·0713
53	1·0638	72	1·0740	91	1·0705
54	1·0646	73	1·0742	92	1·0696
55	1·0653	74	1·0744	93	1·0686
56	1·0660	75	1·0746	94	1·0674
57	1·0666	76	1·0747	95	1·0660
58	1·0673	77	1·0748	96	1·0644
59	1·0679	78	1·0748	97	1·0625
60	1·0685	79	1·0748	98	1·0604
61	1·0691	80	1·0748	99	1·0580
62	1·0697	81	1·0747	100	1·0553
63	1·0702	82	1·0746		

BY NORMAL ALKALI.

Neutral acetates turn red litmus blue, and in estimating acetic acid with normal alkali, we must hence add the latter until the litmus becomes blue, and not as with other acids until the violet shade is produced The acid may also be determined by Pettenkofer's or Kieffer's method.

$$\text{c. c. normal alkali} \times \cdot 060 = C_2H_4O_2$$

One of the best methods for the estimation of acetic acid (C. Mohr's) is to add a weighed amount in excess of precipitated pure calcium carbonate, and allow the acid to become nearly saturated in the cold, then boil to drive off carbonic acid, wash the remainder of the calcium carbonate with hot water, and estimate its amount by dissolving in excess of normal acid and titrating back with normal alkali. This process is applicable to colored liquids, such as impure vinegar, pyroligneous acid, etc., and yields good results.

$$CaCO_3 \times 1{\cdot}2 = C_2H_4O_2$$

The acetic acid in acetates may be estimated by adding phosphoric acid to the salt, and distilling it in the apparatus, Fig. 42.*

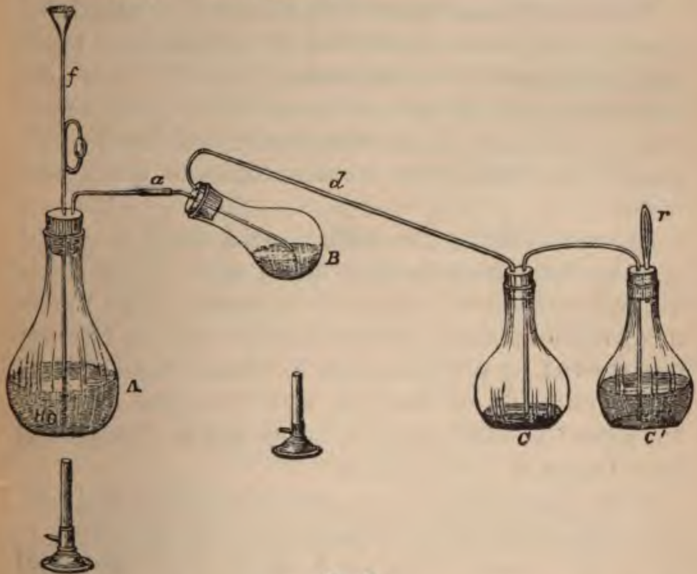

FIG. 42.

The bottle *B* contains the acetate, which is placed in an inclined position, to prevent any of the phosphoric acid from reaching the tube *d* by spattering, and thence passing into the distillate. While the distillation is progressing, steam, which is generated in *A*, passes through *B*, and continues thus to wash out the last traces of the free volatile acids. The funnel-tube *f* is merely a safety-valve.

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* Endemann, Amer. Chemist, vol. vi. 295.

The steam, laden with the acid vapors, passes through *d* into the two flasks *C* and *C′*, connected by tubes, as shown in the figure. These flasks are charged with 25 c. c. of normal soda solution for every 2 to 2½ gms. of the acetate to be determined.

The distillation is generally finished in about one fourth of an hour, when from 20 to 30 c. c. of water have condensed into the flasks *C* and *C′*. After the distillation has fairly commenced, it is only necessary to apply the flame occasionally to *B* for the purpose of preventing the accumulation of condensed water.

Instead of using phosphoric acid, sulphuric acid may be used with perfect safety after it has been diluted with three volumes of water. That under these circumstances no sulphurous acid is formed, was proved by a distillation in which *C* and *C′* contained chloride of barium, which neither at once, nor after the addition of chlorine water, showed the least traces of a precipitate.

If the distillation be considered finished, the rubber connection *a* is opened, and the apparatus is allowed to cool, while air is made to slowly pass through it by sucking at *r*.

If too much water has not been allowed to accumulate at *B*, the tube *d* will become perfectly dry during this operation.

After carefully removing the fluid from the flasks *C* and *C'*, and washing them as well as the connecting tubes repeatedly with fresh water—the wash waters to be added to the fluid—its degree of saturation is determined by normal sulphuric acid solution in the presence of litmus. If, during this process, the fluid has become violet, and the exact quantity of excessively added acid has not been noticed, it becomes necessary to add normal soda solution, drop by drop, until the blue color is restored. This is necessary on account of the alkaline reaction of the neutral acetates. According to Witz,* violet of methylanaline may be used for estimating acetic acid in presence of free mineral acid; free mineral acids color this substance bluish green, while acetic acid has no effect.

Acetates may be estimated by adding normal acid until the violet changes to bluish green. According to Endemann,† this method, "though theoretically an impossibility, was tried, but found to be perfectly valueless."‡

FORMIC ACID.§

PLACE in a flask 5 gms. sodium acetate, 25 c. c. of a 10 % solution of the substance whose content in formic acid is to be ascertained, and 200 c. c. of a 4·5 solution of mercuric chloride. Heat upon th water-bath until the decomposition of the formi acid is complete (1 to 1½ hours), and the mercurou chloride formed has settled completely, leaving th supernatant liquid perfectly clear. The whole solution is now diluted to 500 c. c., filtered, a burett filled with a portion of the fluid, and the mercur remaining in solution determined by finding th number of c. c. required to produce the red precipitate with 1 gm. potassium iodide. (See pag 160.) The strength of the mercury solution bein determined in the same way beforehand, a simpl calculation shows the amount of formic acid.

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* Bulletin de la Société de Rouen, October, 1874; Amer. Chem. July, 1875.

† American Chemist, vol. vi. 296.

‡ See also Hilger, Fres. Zeit. 16, 117.

§ Portes and Ruyssen, Fresenius, Zeitschrift, 16, 250.

TARTARIC ACID.

TABLE.

Specific gravity of solutions of crystallized Tartaric Acid in water. Temp. 15°. *Water at* 15° = 1.*

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·0045	10	1·04692	19	1·0917
2	1·0090	11	1·0517	20	1·09693
3	1·0136	12	1·0565	21	1·1020
4	1·0179	13	1·0613	22	1·1072
5	1·0224	14	1·0662	23	1·1124
6	1·0273	15	1·0709	24	1·1175
7	1·0322	16	1·0761	25	1·1227
8	1·0371	17	1·0813	26	1·1282
9	1·0420	18	1·0865	27	1·1338

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* Gerlach, Specifische Gewichte der Salzlösungen.

TABLE—(*Continued*).

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
28	1·1393	38	1·1959	48	1·2568
29	1·1449	39	1·2019	49	1·2632
30	1·15047	40	1·20785	50	1·26962
31	1·1560	41	1·2138	51	1·2762
32	1·1615	42	1·2198	52	1·2828
33	1·1670	43	1·2259	53	1·2894
34	1·1726	44	1·2317	54	1·2961
35	1·1781	45	1·2377	55	1·3027
36	1·1840	46	1·2441	56	1·3093
37	1·1900	47	1·2504	57	1·3159

FREE tartaric acid is estimated by normal alkali, or it may be determined by Pettenkofer's method.

c. c. normal alkali × ·075 = $C_4H_6O_6$

Acid Potassium Tartrate (*Cream of Tartar*).

Acid potassium tartrate may be estimated by dissolving it in hot water, adding litmus and normal alkali until the violet color appears.

c. c. normal alkali × ·188137 = $C_4H_5KO_6$
" " " × ·1500 = $C_4H_6O_6$

Tartaric acid may be separated from solutions containing it by making the solution somewhat acid by adding acetic acid, then potassium acetate, and, lastly, twice the volume of the solution of alcohol of 95 %. Agitate the solution vigorously, and let it stand an hour. Wash the precipitate with a mixture of two volumes of alcohol and one volume of water, dissolve it in boiling water, and titrate with normal alkali; or add neutral acetate of lead in excess. The tartaric acid is thrown down as lead tartrate, this is washed with a mixture of equal volumes alcohol and water, suspended in water, and H_2S passed through the solution until all lead is precipitated as sulphide. The solution is boiled to expel the excess of sulphydric acid, filtered, and the tartaric acid in the filtrate determined by normal alkali.*

CITRIC ACID.

TABLE.

Specific gravity of solutions of crystallized Citric Acid in water. Temp. 15°. *Water at* 15° = 1.†

Per cent.	Specific Gravity.	Per cent.	Specific Gravity.	Per cent.	Specific Gravity.
1	1·00370	23	1·09300	45	1·19470
2	1·00740	24	1·09720	46	1·19980
3	1·01110	25	1·10140	47	1·20500
4	1·01490	26	1·10600	48	1·21030
5	1·01860	27	1·11060	49	1·21530
6	1·02270	28	1·11520	50	1·22041
7	1·02680	29	1·11980	51	1·22570
8	1·03090	30	1·12439	52	1·23070
9	1·03500	31	1·12880	53	1·23590
10	1·03916	32	1·13330	54	1·24100
11	1·04310	33	1·13780	55	1·24620
12	1·04700	34	1·14220	56	1·25140
13	1·05090	35	1·14670	57	1·25720
14	1·05490	36	1·15150	58	1·26270
15	1·05880	37	1·15640	59	1·26830
16	1·06320	38	1·16120	60	1·27382
17	1·06750	39	1·16610	61	1·27940
18	1·07180	40	1·17093	62	1·2 490
19	1·07620	41	1·17560	63	1·29040
20	1·08052	42	1·18140	64	1·2 600
21	1·08480	43	1·18510	65	1·30150
22	1·08890	44	1·18990	66	1·30710

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* Fleischer, Archiv der Pharmacie, Aug. 1874 ; Fres. Zeit. 13, 328.

† Gerlach, Specifische Gewichte der Salzlösungen.

FREE citric acid is estimated by litmus and normal alkali, or by Pettenkofer's method.

$$\text{c. normal alkali} \times \cdot 070 = C_6H_8O_7, H_2O$$

Citric acid may be separated from solutions containing it by adding neutral lead acetate. The lead citrate is washed with a mixture of equal volumes alcohol and water, suspended in water, and H_2S passed through the solution. After all lead is precipitated, the solution is boiled to drive off excess of sulphydric acid, filtered, and the citric acid in the filtrate determined by normal alkali.* All other acids which are precipitated under similar conditions must first be removed.

SUGAR.

THE class of bodies called by this name may be divided into two groups:

1. Those containing $C_6H_{12}O_6$ (glucoses).
   Glucose, dextrose or dextroglucose.
   Fruit-sugar, lævulose or lævoglucose.
   Galactose.
2. Those containing $C_{12}H_{22}O_{11}$
   Saccharose or cane-sugar.
   Lactose or milk-sugar.
   Melezitose.
   Melitose.
   Mycose.
   Synanthrose.

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* Fleischer, Archiv der Pharmacie, Aug. 1874; Fres. Zeit. 13, 328.

The members of the second group may be converted into those of the first by boiling with dilute acid for twenty minutes. Two members of the first group are produced by the decomposition of one of the second, water being taken up. For example:

$$\overset{\text{Cane-sugar.}}{C_{12}H_{22}O_{11}} + H_2O = \overset{\text{Dextrose.}}{C_6H_{12}O_6} + \overset{\text{Lævulose.}}{C_6H_{12}O_6}$$

Estimation of Sugar by Fehling's Method.

The sugar must be a member of the first group. If cane-sugar, milk-sugar, etc., are to be estimated, they must first be boiled with dilute sulphuric or hydrochloric acid for twenty or thirty minutes, and the acid neutralized before proceeding with the analysis.

The method depends upon the fact that alkaline solutions of copper salts are reduced by the glucoses, cuprous oxide being thrown down in proportion to the amount of sugar present.

One equivalent of pure grape-sugar reduces five equivalents of cupric oxide to cuprous oxide.

Copper solution: Made by dissolving 34·6333 gms. pure copper sulphate in water, and adding to a solution of 173 gms. of Rochelle salt in 480 c. c. of sodium hydrate, sp. gr. 1·14, and diluting to a litre. One c. c. of such a solution is equal to ·005 gms. pure grape-sugar. It must be kept in a dark place, and must not be allowed to absorb carbonic acid. The analysis is made by running the sugar solution from a burette into a measured portion of the copper solution until all the copper is precipitated, and blue color of the solution has disappeared.

If the sugar solution be dark-colored, it may be rendered colorless by adding a little lime-water and some bone-black, boiling and filtering. The solution of the sugar is in all cases made up to a definite volume, and a portion poured into the burette for the analysis. It must not contain more than 1 % sugar, and is better if more dilute. Ten c. c. of the copper solution are measured into a beaker or porcelain dish, diluted four or five times, and heated to boiling. The sugar solution is then run in until the copper solution has lost all color, and the copper is all precipitated as red cuprous oxide. This point is somewhat difficult to hit with exactness at the first trial; and when the end is apparently reached, it is a good plan to filter a small portion of the liquid by means of the filtering pipette, acidify it with a few drops of acetic acid, and add a drop of potassium ferrocyanide. If any copper remains in solution, this gives a reddish brown coloration to the fluid.

Calculation: Suppose 2 gms. sugar were taken, dissolved in water, and diluted to 500 c. c.; 10 c. c. copper solution require 13·5 c. c. of the sugar solution; 13·5 c. c. therefore contain $10 \times \cdot005 = \cdot05$ gms. sugar, and 500 c. c. contain $\frac{500}{13.5} \times \cdot05 = 1\cdot8518$ gms. pure sugar, or 92·59 %.

Another method is to add the copper solution, prepared as above, in excess to the sugar solution, heat to boiling, and filter through asbestos. The cuprous oxide is washed with hot water, placed in a flask containing ferric sulphate, which dissolves it, becoming reduced to ferrous sulphate, and the amount of ferrous salt produced is measured by permanganate. While the cuprous oxide is digested with the ferric sulphate, a stream of hydrogen or carbon dioxide should be run through the flask.

$$\text{c. c. } \tfrac{n}{10} \text{ permanganate} \times \cdot 0036 = C_6H_{12}O_6$$

Another and perhaps the best method is one proposed by Fahlberg. An excess of Fehling's solution is added, and the copper in excess found by precipitating with the battery.

*By Mercuric Cyanide.**

Mercuric cyanide in alkaline solution is reduced by grape-sugar to metallic mercury in the proportion of one part grape-sugar to 4 parts mercuric cyanide.

Mercuric cyanide solution: Made by dissolving 10 gms. mercuric cyanide in 600 c. c. water, adding 100 c. c. sodium hydrate, sp. gr. 1·145, and diluting to a litre.

Forty c. c. of the cyanide solution are poured into a beaker and brought to a boil, and then the sugar solution added from a burette until a drop of the supernatant fluid no longer produces a brown spot when placed upon filter-paper and held over a watch-glass containing strong ammonium sulphide. The 40 c. c. mercuric cyanide solution are equal to ·1000 gms. $C_6H_{12}O_6$.

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* Knapp, Fres. Zeit. 10, 395; Liebig's Annalen, 154, 252.

PHENOL (CARBOLIC ACID).*

WHEN bromine is added to phenol in excess, tribromphenol is formed according to the following equation:

$$C_6H_5,OH + 6Br = C_6H_2Br_3,OH + 3HBr$$

The tribromphenol is nearly absolutely insoluble. An excess of bromine water (whose strength has been determined by adding an excess of potassium iodide to a measured portion, and determining the liberated iodine with sodium thiosulphate) is added, and, after the separation of the tribromphenol, an excess of potassium iodide, and the iodine set free, which corresponds with the excess of bromine, titrated with sodium thiosulphate. The calculation is 480 bromine = 94 phenol.

Instead of using bromine water for the titration, Koppeschaar uses a mixture of sodium or potassium bromide and bromate in the proportion of 5 molecules bromide and 1 bromate. Such a solution added to hydrochloric acid is decomposed into sodium or potassium chloride and free bromine.

$$5KBr + KBrO_3 + 6HCl = 6\ Br + 3H_2O + 6KCl$$

Such a mixture is easiest obtained by adding bromine in excess to a solution of sodium or potassium hydrate, and evaporating the solution to dryness. Theoretically, for ·1 gm. phenol, ·7606 gm. of the mixture of potassium bromate and bromide, or ·751 gm. of the mixture of sodium salts, is required.

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* Koppeschaar, Fresenius, Zeitschrift, 15, 233.

The solutions used by Koppeschaar are empirical, but may just as well be decinormal.

1. Decinormal sodium thiosulphate.

2. A solution of the mixture of sodium bromide and bromate of such strength that 50 c. c., when heated with an excess of potassium iodide and hydrochloric acid, require just 50 c. c. sodium thiosulphate.

3. A solution of potassium iodide containing 125 gms. salt per litre.

Four gms. of the oil are dissolved in water by shaking, and made up to 1 litre; ·25 c. c. of this solution are placed in a stoppered flask, and 75 c. c. of the sodium bromide bromate solution, and 5 c. c. concentrated hydrochloric acid added, and the flask closed and shaken. After 15 minutes, the flask is opened, and 10 c. c. of the potassium iodide solution added, the flask closed, and again shaken, finally the contents poured into beaker, the flask washed out, and the iodine determined by the $\frac{n}{10}$ thiosulphate.

c. c. bromide bromate – c. c. thiosulphate × ·001567
= phenol.

COMPOUND ETHERS

May be determined by heating them with an excess of normal alkali in a stoppered bottle. The are decomposed by this means into an acid which combines with a part of the alkali and an alcohol. The excess of alkali is measured by normal acid, and the amount of ether calculated from the alkali which was saturated. The ether to be so measured must of course contain no free acid dissolved in it.

CHLORAL HYDRATE

May be estimated like a compound ether, being decomposed by normal alkali into chloroform and formic acid.*

$$CCl_3CHO + H_2O + NaOH = CHCl_3 + HCOONa + H_2O$$

An excess of normal NaOH is added, and the excess found by normal acid. Not less than 4 gms. chloral hydrate must be used. If it contains free HCl, the solution must be first shaken with pure $CaCO_3$. The following equation gives the chloral hydrate in any case:

$$x = \frac{(a - b)\ 165{\cdot}5}{1000}\ \text{gms.}$$

a = normal NaOH taken.
b = " HCl "

The amount of chloral may also be found by adding solution of sodium or potassium hydrate to 25 gms. of the chloral hydrate, contained in a graduated tube. After the lapse of a few hours, the decomposition is complete, the chloroform has settled to the bottom, and the volume is read off, and from this the amount of chloral hydrate calculated. (K. Muller.)*

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* Fres. Zeit. 12, 319.

CHLORINE COMPOUNDS.

CHLORINE.

FREE chlorine may be estimated by passing the gas into a solution of potassium iodide, and determining the iodine set free by sodium thiosulphate and starch.

$$\text{c. c. } \tfrac{n}{10} \text{ thiosulphate} \times \cdot 0035457 = \text{Cl}$$

HYDROCHLORIC ACID.

WHEN the acid is pure, its strength may be found by taking the specific gravity. Comparison with the following table shows the percentage of HCl.

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* Chem. News, xxiii. 113.

TABLE.

Specific gravity of solutions of Hydrochloric Acid. Temp. 15° (*Ure*).

Specific Gravity.	Per cent HCl.	Specific Gravity.	Per cent HCl.	Specific Gravity.	Per cent HCl.
1·2000	40·777	1·1328	26·913	1·0637	13·049
1·1982	40·369	1·1308	26·505	1·0617	12·641
1·1964	39·961	1·1287	26·098	1·0597	12·233
1·1946	39·554	1·1267	25·690	1·0577	11·825
1·1928	39·146	1·1247	25·282	1·0557	11·418
1·1910	38·738	1·1226	24·874	1·0537	11·010
1·1893	38·330	1·1206	24·466	1·0517	10·602
1·1875	37·923	1·1185	24·058	1·0497	10·194
1·1857	37·516	1·1164	23·650	1·0477	9·786
1·1846	37·108	1·1143	23·242	1·0457	9·379
1·1822	36·700	1·1123	22·834	1·0437	8·971
1·1802	36·292	1·1102	22·426	1·0417	8·563
1·1782	35·884	1·1082	22·019	1·0397	8·155
1·1762	35·476	1·1061	21·611	1·0377	7·747
1·1744	35·068	1·1041	21·203	1·0357	7·340
1·1721	34·660	1·1020	20·796	1·0337	6·932
1·1701	34·252	1·1000	20·388	1·0318	6·524
1·1681	33·845	1·0980	19·980	1·0298	6·116
1·1661	33·437	1·0960	19·572	1·0279	5·709
1·1641	33·029	1·0939	19·165	1·0259	5·301
1·1620	32·621	1·0919	18·757	1·0239	4·893
1·1599	32·213	1·0899	18·349	1·0220	4·486
1·1578	31·805	1·0879	17·941	1·0200	4·078
1·1557	31·398	1·0857	17·534	1·0180	3·670
1·1537	30·990	1·0838	17·126	1·0160	3·262
1·1515	30·582	1·0818	16·718	1·0140	2·854
1·1494	30·174	1·0798	16·310	1·0120	2·447
1·1472	29·767	1·0778	15·902	1·0100	2·039
1·1452	29·359	1·0758	15·494	1·0080	1·631
1·1431	28·951	1·0738	15·087	1·0060	1·124
1·1410	28·544	1·0718	14·679	1·0040	0·816
1·1389	28·136	1·0697	14·271	1·0020	0·408
1·1369	27·728	1·0677	13·863		
1·1349	27·321	1·0657	13·456		

ACIDIMETRIC METHOD.

If the solution be free from salts of the heavy metals whose neutral salts redden litmus, the free acid may be measured by adding litmus, and then normal alkali in the usual way.

c. c. normal acid × ·036457 = HCl

In a solution containing salts of the heavy metals the free acid must be determined by Kieffer's method.

HYDROCHLORIC ACID AND CHLORIDES.

BY SILVER NITRATE.

THE process is the reverse of the silver estimation. The chloride in neutral or faintly alkaline solution is precipitated by the addition of $\frac{n}{10}$ silver nitrate, 2 drops of potassium chromate solution having been previously added. The precipitation is completed when the red silver chromate makes its appearance. Silver chromate is slightly soluble. It dissolves in 6666·6 parts water at 17·5°, and in 3704 parts boiling water.* For this reason, the solutions in which chlorine is to be estimated must not be too dilute, and the titration should be performed at the ordinary temperature. Where great accuracy is necessary, it is best to add two drops potassium chromate to some distilled water, then sufficient silver nitrate to show the red coloration; the chloride to be estimated dissolved in a small bulk of water is then added, and $\frac{n}{10}$ silver nitrate run in until the same color again appears.

c. c. $\frac{n}{10}$ silver nitrate × ·0035457 = Cl
" " " " × ·0036457 = HCl

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* Mohr, Titrirmethode, p. 395.

IN AN ACID SOLUTION.

In this case, the silver nitrate solution is added, shaking violently after each addition, and allowing the precipitate to settle until it ceases to produce a precipitate in the clear solution. Or,

By means of the filtering pipette, find the neutral point. (See Silver.)

Chlorine may also be estimated by any of the other methods given, for the determination of silver. It is only necessary to add an excess of $\frac{n}{10}$ silver nitrate to the solution, filter, and determine the excess of silver in the filtrate.

BY MERCURIC NITRATE.

This method was first employed by Liebig for the determination of chlorine in urine. It is grounded upon the fact that mercuric nitrate is precipitated by urea or sodium phosphate. In presence of sodium chloride, however, no precipitate appears until a sufficient quantity of mercuric nitrate has been added to satisfy the chlorine, which combines with the mercury, forming mercuric chloride. As soon as the chlorine has all combined with the mercury, a further addition of mercuric nitrate produces a white precipitate.

Both of these precipitates are, however, soluble in dilute acids, and since it is impossible to obtain a neutral solution of mercuric nitrate, the method is not by any means exact.

Mohr, acting upon a suggestion of Kieffer's, has substituted potassium ferricyanide for the urea or sodium phosphate, with the best results, the precipitate which is obtained after all the chlorine has combined with the mercury being entirely insoluble in the slightly acid liquid.

Solution of mercuric nitrate: This must be pure, and contain no other metals which are precipitated in acid solution by potassium ferricyanide. It is prepared as follows: The purest mercury that can be obtained is dissolved in nitric acid and allowed to crystallize. The crystals are nearly pure, the impurities being contained in the mother liquor. They are dissolved in a little water and nitric acid, the solution brought to boiling, and strong nitric acid added until red fumes are no longer given off. The solution is evaporated to a syrupy consistence, dissolved in water, and diluted to proper strength. In diluting this solution, it is always necessary to add a little nitric acid to the water, otherwise a precipitate of basic mercuric nitrate is formed. Care should be taken, however, not to have more free nitric acid present than is sufficient to keep the mercury all in solution. The strength is best found by titrating against pure sodium chloride. A few small crystals of pure potassium ferricyanide are added to the solution to be titrated, and the mercuric nitrate solution run in until the precipitate produced no longer redissolves upon shaking.

$$\text{c. c. } \tfrac{n}{10} \text{ mercuric nitrate} \times \cdot 0035457 = \text{Cl}$$

The method is inapplicable in presence of any of the metals which are precipitated by potassium ferricyanide. The method is good, but not quite so reliable as the method with silver nitrate with potassium chromate as indicator, and possesses no advantages over it.

HYPOCHLORITES.

Commercial hypochlorites are products obtained by the action of chlorine upon the carbonates or hydrates of the alkaline or alkaline earth metals. The following formula shows the composition of pure "chloride of lime:"

$$Ca_3H_6O_6Cl_4$$

Whatever be its composition in the dry state, however, when brought into solution, it seems to form calcium hypochlorite, calcium chloride, calcium hydrate, and water.

$$Ca_3H_6O_6Cl_4 = CaCl_2O_2 + CaCl_2 + Ca(OH)_2 + 2H_2O$$

"Chloride of soda," or Labarraque solution, contains

$xNa_2Cl_2O_2 + xNaCl + xNa_2CO_3$, Chloride of potash, or "*Eau de Javelle*," $xK_2Cl_2O_2 + xKCl + xK_2CO_3$

When such solutions are heated with an acid, all the chlorine is given off in the form of gas.

$$CaCl_2O_2 + CaCl_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + 4Cl$$

The bleaching or oxidizing effect of hypochlorites is therefore equal to twice the amount of chlorine contained in the hypochlorite. It is usual to estimate the bleaching effect upon this basis. In England, the practice is to estimate the percentage of chlorine as double the amount contained in the hypochlorite, since one atom oxygen in bleaching power is equal to two atoms chlorine, or $Cl_2O = 4Cl$. In France, the estimate is based upon a scale established by Gay-Lussac, according to which, the strength is measured by the number of litres of chlorine at 0°C ·760 mm. barometer, given off by 1 kilogramme "chloride of lime." If chloride of lime has a strength of 99°, according to the French system, it means that 1 kilogramme, heated with acid, gives off 99 litres chlorine, or as 1 litre chlorine weighs 3·177 gms., 1 kilogramme would contain $99 \times 3{\cdot}177 = 314{\cdot}523$ gms., or 31·425 % chlorine. Therefore, degrees × ·3177 = per cents; per cents ÷ ·3177 = degrees.

BY SODIUM ARSENITE.

Arsenious acid in alkaline solution is oxidized by free chlorine or hypochlorites to arsenic acid.

$$As_2O_3 + CaCl_2O_2 = As_2O_5 + CaCl_2$$

Since the two atoms of oxygen taken from the calcium hypochlorite are equal in oxidizing power to 4 atoms chlorine, we have

$$\begin{aligned} As_2O_2 &= 4Cl \\ 198{\cdot} &= 141{\cdot}828 \end{aligned}$$

Hence the decinormal solution of sodium arsenite described on page 59, containing 4·95 gms. As_2O per litre, will be equivalent to a solution containing

3·5457 gms. chlorine per litre, or 1 c. c. = ·0035457 chlorine.

The method consists in delivering the arsenite into the solution of hypochlorite until a drop brought in contact with iodized starch-paper shows no further blue color.

The iodized starch-paper is made by dissolving 3 gms. starch in 250 c. c. of boiling water, adding 1 gm. potassium iodide and 1 gm. crystallized sodium carbonate, and diluting the whole to 500 c. c. Strips of filter-paper are dipped in the solution and used in the damp state.

If chloride of lime is to be examined, the process is as follows: The sample is rapidly and thoroughly mixed, and 10 gms. weighed out into a mortar. It is rubbed with considerable water by means of the pestle, and after standing quietly for a few minutes to allow the larger particles to settle, the still turbid fluid poured into a litre flask. Rub the chloride of lime remaining in the mortar with more water, and repeat this treatment until the entire amount has been brought without loss into the litre flask; mix thoroughly by shaking the flask, fill to the mark with water, and take out 100 c. c. of the turbid liquid for analysis.

A clear solution containing all the available chlorine may also be obtained by dissolving the sample in water, heating nearly to boiling, adding twice as much crystallized sodium carbonate, filtering, and washing the precipitate until the washings no longer produce a blue spot upon iodized starch paper.*

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* Smyth, Chem. News, xxiv. 75.

The solution of arsenious acid may also be made by dissolving the proper amount in 15 c. c. glycerine by the aid of heat, adding some HCl, and diluting to a litre. To make the analysis with this solution, 10 c. c. are taken out, a drop of solution of indigo sulphate added, and the turbid solution of the chloride of lime run in until the blue color of the indigo is discharged.*

Where the strength of bleaching powder is to be determined in degrees, it is usual, for technical purposes, to use a solution of arsenite, containing 4·436 gms. As_2O_3 per litre. Each c. c. of such a solution is equal to 1 degree when 1 gm. chloride of lime is taken for analysis.

If we take 1 gm. of the bleaching powder for analysis, and wish to let the number of c. c. arsenite used = %, we must use a solution of arsenite containing 13·96 gms. As_2O_3 per litre. The solution containing 4·95 gms. As_2O_3 per litre answers the same purpose if ·35457 gms. instead of 1 gm. be taken for the analysis.

When chloride of lime is kept for a long time, or is exposed to an elevated temperature, the calcium hypochlorite is partly decomposed, calcium chlorate and calcium chloride being formed.

$$3CaCl_2O_2 = Ca(ClO_3)_2 + 2CaCl_2$$

Neither calcium chlorate nor chloride is of any value for bleaching purposes, however, and such a bleaching powder is less valuable than one recently made. The arsenite solution, however, is not oxidized in alkaline solution by calcium chlorate, and hence this estimation furnishes a true indicator of the value for bleaching purposes. The methods of Otto and Bunsen, to be described presently, are only applicable for samples of bleaching powder which contain no chlorate, or they may be used for determining chlorate and hypochlorate together. A second estimation by arsenious acid gives the hypochlorite, and, subtracting the second from the first, gives the chlorate present.

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* Davis, Chem. News, xxvi. 25.

BUNSEN'S METHOD.

20 c. c. of the turbid solution of bleaching powder are poured into an excess of potassium iodide, acidified slightly with hydrochloric acid, and the iodine estimated by $\frac{n}{10}$ thiosulphate and starch. Or the bleaching powder may be distilled with hydrochloric acid in a flask, the chlorine received in a solution of potassium iodide, and the iodine set free, titrated with $\frac{n}{10}$ thiosulphate and starch.

$$\text{c. c. } \tfrac{n}{10} \text{ thiosulphate} \times \cdot 0035457 = \text{Cl.}$$

OTTO'S METHOD.

A quantity of ferric sulphate is weighed into a beaker, dissolved in water, some dilute sulphuric acid added, and the turbid solution of bleaching powder run in from a Gay-Lussac burette until a drop of the liquid gives no blue precipitate with potassium ferricyanide.

$$\text{Ferrous sulphate} \times \cdot 12754 = \text{Cl.}$$

FRESENIUS' MODIFICATION OF OTTO'S METHOD.

Weigh off accurately about 15 gms. iron wire, dissolve in hydrochloric acid in a flask through which hydrogen or carbon dioxide is passing, allow to cool, and dilute to about 200 c. c. Oxidize the iron with the turbid solution of bleaching powder run in from a burette, and calculate the proportion. 56 : 35·457 :: the quantity of iron used : x. x = the chlorine in the amount of chloride of lime used. This calculation may be dispensed with by the application of the following formula, in which the carbon in the piano-forte wire is taken into account.

Multiply the weight of the piano-forte wire by 6313 and divide the product by the number of c. c. used of the solution of chloride of lime ; the result expresses the percentage of chlorine by weight.

CHLORIC ACID AND CHLORATES.

BY OXIDATION OF FERROUS SALTS.

If chloric acid or a chlorate is added to an acid solution of ferrous sulphate, the following reaction takes place :

$$12FeSO_4 + 2KClO_3 + 7H_2SO_4 = 6Fe_2(SO_4)_3 + K_2SO_4 + 6H_2O + 2HCl$$

The chlorate is dissolved in water, solution of ferrous ammonium sulphate in excess added, then some sulphuric acid, and the solution heated for some time. The excess of ferrous salt is then found by bichromate. It is best to conduct the operation in a flask through which hydrogen or carbon dioxide is passing, to prevent oxidation of the ferrous salt by the oxygen of the air.

$$\text{Ferrous ammonium sulphate} \times \cdot 05212 = KClO_3$$

BY DIGESTION WITH KI AND HCl.

When a chlorate is digested with KI and HCl in a stoppered flask, it is decomposed, and iodine is set free, which may be measured by starch and $\frac{n}{10}$ thiosulphate.

$$KClO_3 + 6KI + 6HCl = 7KCl + 3H_2O + 6I$$

$$\text{c. c. } \frac{n}{10} \text{ thiosulphate} \times \cdot 0020432 = KClO_3$$

BROMINE.

Bromine, added to a solution of potassium iodide, sets free an equivalent of iodine, which may be measured by $\frac{n}{10}$ thiosulphate and starch. Care must be taken to use an excess of potassium iodide.

$$\text{c. c. } \frac{n}{10} \text{ thiosulphate} \times \cdot 0079952 = Br$$

HYDROBROMIC ACID AND BROMIDES.

In the absence of chlorides, iodides, and cyanides, the amount of bromine present as hydrobromic acid or metallic bromide may be found by precipitating with $\frac{n}{10}$ silver nitrate. The precipitate being quite as insoluble as silver chloride, either of the methods given under hydrochloric acid answer equally well for hydrobromic.

$$\text{c.c. } \tfrac{n}{10} \text{ silver nitrate} \times \cdot 0079952 = \text{Br}$$

ESTIMATION OF BROMIDES IN PRESENCE OF CHLORIDES.

Where great accuracy is required, the estimation must be made by gravimetric methods. When approximate results will answer, either of the following methods may be employed:

REIMANN'S METHOD.

When chlorine water is added to a bromide, it first sets all the bromine free, and then combines with it, forming bromine chloride, which has much less color than bromine itself.

Mix the liquid containing the bromine in combination with an alkaline metal in neutral solution with enough chloroform to leave a piece the size of a hazel-nut undissolved. The solution should be contained in a stoppered bottle. Run chlorine water from a burette into the fluid, shaking after each addition. The globule of chloroform at first becomes yellow, then orange, yellow again, and finally "yellowish white." This point is difficult to hit with any precision, unless we have a standard of color for comparison. This standard is made as follows: Take a weighed quantity of pure potassium bromide, dissolve in water, pour into a bottle, and add some chloroform, and then add a quantity of chlorine water from the burette, exactly sufficient to form BrCl with the bromine of the potassium bromide. This quantity is 2 atoms chlorine to 1 atom bromine, and, as the strength of the chlorine water is known, may easily be calculated. A solution of potassium chromate is then made of such strength that it corresponds in color with the globule of chloroform, and a portion of this solution is taken for comparison in subsequent analyses.

The solution of chlorine in water is standardized by adding a measured volume to an excess of potassium iodide, and determining the liberated iodine by $\frac{n}{10}$ thiosulphate. The burette to contain it must be covered with a case of black paper that can be slipped off and on, to protect it from the decomposing action of the light.

By this method Reimann obtained ·0180 instead of ·0185—·055 instead of ·059—·0112 instead of ·0100.

HIMES' METHOD, MODIFIED BY FRESENIUS.

The bromine is liberated by chlorine water, and a quantity of chloroform or carbon bisulphide added to absorb it. The solution is thoroughly shaken after each addition of chlorine water, to allow the chloroform to absorb the liberated bromine. The chlorine water is added as long as the chloroform darkens in color, and the amount of bromine found by comparing the color with a chloroformic solution of bromine of known strength. The amount of bromine must be approximately known, and the analysis must be performed rapidly and away from strong light. The amount of chloroform taken for the analysis and for making the solution of bromine for comparison should be equal.

ESTIMATION OF BROMIDES IN PRESENCE OF CHLORIDES AND IODIDES.

When chlorine water is added to a solution containing an iodide, iodine is set free, and then combines with the excess of chlorine, forming ICl_5, which is colorless, and is immediately decomposed by water into iodic and hydrochloric acids, also colorless. If bromine be present, and the solution is dilute, it takes the place of the chlorine and forms IBr_5, which is likewise colorless.

The analysis is conducted in the same way as in Reimann's method for bromine in presence of chlorine. The fluid must, however, be dilute, and must not contain more than 1 part potassium bromide to 13,000 of water. A globule of chloroform is added, and then chlorine run in as before. The iodine is set free at first, and gives a blue color to the chloroform, which gradually passes through violet, and then suddenly becomes colorless. At this point, all the iodine has been converted into iodic acid, and the bromine is present as HBr. The amount of chlorine water used thus far is noted, and then more run in. The bromine is now set free, and then combines with the excess of chlorine to form BrCl, until the "yellowish white" color is produced in the globule of chloroform. The second portion of chlorine water is a measure of the bromine present, 2 equivalents chlorine being equal to 1 equivalent bromine.

BROMIC ACID.

Determined like chloric acid.

IODINE.

IODINE in the free state is estimated by dissolving in potassium iodide, and titrating with $\frac{n}{10}$ thiosulphate.

HYDRIODIC ACID AND IODIDES BY CHLORINE WATER AND CHLOROFORM.

When chlorine water is added to an iodide, the iodine is first set free, and then combines with the excess of chlorine, ICl_5 being the final product. The lower chlorides of iodine, as well as iodine itself, color chloroform violet; the pentachloride is, however, colorless, and is decomposed by water into iodic and hydrochloric acids, also colorless. The chlorine-water is added to a solution containing the iodine, together with two or three c. c. chloroform, until the color at first produced in the chloroform just disappears. The strength of the chlorine water is determined by running a measured amount into potassium iodide, and measuring the liberated iodine by $\frac{n}{10}$ thiosulphate. The results are accurate.

Mohr's Modification of the above Process.

Chlorine water is added in excess until all yellowish color has disappeared, and a drop of the solution gives no blue color with starch. Sodium bicarbonate is now added until the solution is alkaline, and then an excess of potassium iodide. The excess of chlorine sets free an equivalent amount of iodine, which is measured by starch and $\frac{n}{10}$ thiosulphate. Mohr obtained by this method ·010109 gm. iodine instead of ·01 gm.

BY DISTILLATION WITH FERRIC SULPHATE.

When potassium iodide is heated with an acid solution of ferric sulphate, ferrous sulphate is formed and all the iodine is set free.

$$2Fe_2(SO_4)_3 + 4KI = 4FeSO_4 + 2K_2SO_4 + 4I$$

The iodide is heated with the acid solution of ferric sulphate in a flask provided with a perforated cork and wide glass tube nearly touching the surface of a solution of potassium iodide contained in a U tube, into which the tube is fitted by a perforated cork. A piece of magnesite should be placed in the flask along with the iodide. The acid acts upon this slowly, setting free a slow current of carbon dioxide, which prevents regurgitation, and also helps to carry over the vapor of iodine. The tube which conducts the iodine into the potassium iodide must be tolerably wide if much iodine is to be distilled off, otherwise this may condense and completely close it.

When the solution has been boiled for some minutes, and all the iodine seems to be driven over, take away the lamp, disconect the apparatus, and pour the solution of iodine into a beaker, wash out the tube, and pour into it a little fresh potassium iodide and a few drops of starch, then reconnect the apparatus, and boil the liquid for a few minutes. If the solution turns blue, it shows that all the iodine has not been expelled, and the distillation must be continued a short time longer. Both fluids are then mixed, and the iodine determined by $\frac{n}{10}$ thiosulphate. Since for each equivalent of iodine set free, one equivalent of ferrous sulphate is formed, by measuring the amount of this substance by $\frac{n}{10}$ permanganate, we can also determine the amount of iodine.

c. c. $\frac{n}{10}$ thiosulphate or permanganate × ·012685 = I

The above method of distillation may be used for separating iodine from iodides in presence of chlorides. Of course no substance capable of giving off chlorine in contact with hydrochloric acid should be present.

PISANI'S METHOD.

This method is based upon the fact that in solutions containing chlorides, bromides, and iodides, the iodine is precipitated completely by silver nitrate before the chloride begins to come down.

One half c. c. of the solution of starch iodide (see Silver) is added to the mixed chloride and iodide, and then $\frac{n}{10}$ silver solution run in until the blue color of the starch iodide is destroyed. The number of c. c. of silver nitrate used, minus that equivalent to $\frac{1}{2}$ c. c. starch iodide, is a measure of the iodine contained in the mixture.

$$\text{c. c. } \tfrac{n}{10} \text{ silver nitrate} \times \cdot 012685 = \text{I}$$

Fresenius obtained by this method with pure KI 99·31 % instead of 100; with pure KI and twice the amount of sodium chloride, 99·85 % instead of 100; KI + 100 times as much NaCl, 100·26 % instead of 100; KI + twice the amount of KBr, 99·65 % instead of 100.

BY PALLADIOUS CHLORIDE.*

When palladious chloride or nitrate is added to the solution of an iodide, it is completely precipitated as palladious iodide, which is insoluble in dilute acid.

Palladious chloride: This is prepared by dissolving metallic palladium in nitro-muriatic acid, and evaporating to dryness on the water-bath. It is dissolved in water, the strength found by titration against the solution of potassium iodide to be described presently, and diluted until it is equal to it in strength.

Potassium iodide: This is made by dissolving 1·3085 gms. pure potassium iodide in water, and diluting to a litre; 1 c. c. = ·001 gm. I.

The solution, which should not contain more than ·0500 gms. iodine, is diluted somewhat, and warmed by placing the bottle containing it in warm water. The solution of palladious chloride is run in, shaking violently after each addition until no more precipitate is produced in a portion of the clear supernatant liquid. Toward the end of the process, the fluid should be allowed to stand a few minutes after each addition before testing. The filtering pipette may be used to assist in finding the proper point. It is best to take the first analysis as a guide, and make a second, adding nearly the whole amount of palladious chloride solution necessary at once.

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* Kersting, Liebig's Annalen, 87, 25.

$$\text{c. c. palladious chloride} \times \cdot 001 = \text{I}$$

The iodine must always be present as hydriodic acid or a metallic iodide, and never in the free state or as iodic acid. Dilute hydrochloric, sulphuric, phosphoric, nitric, and acetic acids, and neutral potassium, sodium, and ammonium salts of these acids, zinc chloride, calcium chloride, sugar, uric acid, etc., do not interfere; but free chlorine, bromine, iodine, or cyanogen, much nitric acid in a hot solution, and sulphurous acid, are objectionable.

The palladious iodide should be collected by allowing the solutions to deposit in a cylinder. It is heated to redness in a platinum or porcelain crucible, by which the iodine is expelled, and the palladium may be used in preparing new solutions.

All the methods thus far given under this heading are applicable in presence of chlorides and bromides. If the solution contains only iodine, it may be estimated by any one of the methods under chlorine.

IODIC ACID.

Determined like chloric acid.

PART III.

ESTIMATION OF CARBON IN LOW STEELS.

WHEN steels containing less than about ·75 % carbon are dissolved in nitric acid, the solution has a brownish-red color, the shade of which depends upon the amount of combined carbon contained in it. One gm. of the steel is dissolved in nitric acid, and the color of the solution compared with a series of tubes containing solutions which correspond in color to a solution of 1 gm. steel, containing ·02, ·04, ·06, ·08, etc., % carbon. The tubes are arranged in a rack (Fig. 43), they are ⅝ of an inch in diameter, and 3½ inches in length, filled with water and alcohol, colored with coffee, and hermetically sealed. The solution in the tube to the left has its color to correspond exactly with one produced by one gramme of iron containing ·02 per cent of combined carbon dissolved in 15 c. c. of nitric acid. The solution in the tube next to it has its color to correspond with one produced by the same quantity of iron, but containing ·04. per cent combined carbon, and so with each of the other tubes, increasing ·02 per cent of carbon in regular succession to the right, the last reaching ·3 per cent as indicated by the figures on the upper rail of the instrument.

On the back of the instrument, and for the purpose of partially screening the light, and allowing the different shades of color to be distinctly discerned, there is tightly stretched between the rails some fine white parchment-paper. This screen is not shown in the cut, but it serves a very important purpose.

The process is conducted as follows: One gm. of the finely-divided metal is put into a tube of about 1½ inches in diameter and 10 inches long, and digested for fifteen or twenty minutes in 10 c. c. nitric acid of a little more than 1·20 sp. gr., and free from chlorine. The solution is then cautiously poured into a beaker, and a small portion of metal which remains undissolved and adheres to the bottom of the tube, is treated with 5 c. c. of fresh acid, and exposed to a gentle heat till completely dissolved and added to the other. The contents of the beaker, when sufficiently cool, are filtered through two thicknesses of German filtering-paper (not previously moistened, and of a diameter not exceeding 4½ inches) into a tube about 5 inches long, and of precisely the same diameter as those in the instrument.

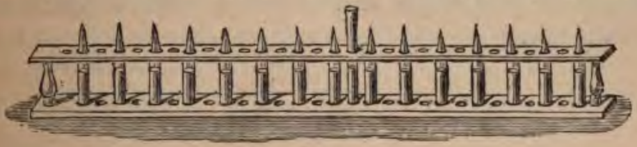

FIG. 43.

After the filtered solution has remained for some minutes at the temperature of the atmosphere, and its color become fixed, the tube is placed in the instrument, and the carbon determined by a comparison of shades. The determination may be made readily as close as ·01 per cent.

Heat should not be applied in the first instance to facilitate the solution of the metal, because a high temperature is apt to cause a slight loss of color. Two thicknesses of paper are taken because one alone is liable to break. If the metal to be examined contains more than ·30 per cent of carbon, ·5 gm. or less of it may be taken, or the solution may be diluted with an equal volume or more of water, and the proper allowance made; on the other hand, if the metal contains a very small per cent of carbon, 2 gms. of it may be taken. As a rule, the instruments are kept in the dark, except when in actual use.*

DISSOLVED OXYGEN IN WATER.

BY FERROUS SULPHATE (MOHR).

WHEN an acid solution of ferrous sulphate is poured into water containing dissolved oxygen, it is not perceptibly oxidized. If the solution be made alkaline, however, the oxygen is completely absorbed, and upon again acidifying, an amount of ferric sulphate is produced equivalent to the dissolved oxygen of the water.

The water to be tested is placed in a bottle, provided with a carefully-ground stopper, and a weighed amount of iron wire dissolved in sulphuric acid, or of ferrous ammonium sulphate dissolved in water, is added. The bottle is then filled with carbon dioxide by placing the end of a tube connected with an apparatus evolving a rapid current of the gas through the neck. An excess of sodium hydrate is then added, the bottle quickly closed, shaken, and allowed to stand for ten or fifteen minutes. The stopper is then taken out, and an excess of sulphuric acid added, after which the fluid is titrated by $\frac{n}{10}$ permanganate for excess of ferrous salt. In filling the bottle with carbon dioxide, the gas must not be allowed to run into the bottle longer than is necessary to fill it, as otherwise a part of the oxygen dissolved in the water will diffuse into it, and the results obtained will be too low.

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* Britton, Chem. News, xxii. 101.

Ferrous ammonium sulphate $\times \cdot 020408 =$ oxygen.

BY SODIUM HYPOSULPHITE.[*]

Solution of sodium hyposulphite rapidly takes up oxygen from a substance containing it, and may be used for estimating oxygen dissolved in water. The following description of the process is taken from an abstract published in the *Journal of the Chemical Society*, 1873, p. 936:

Preparation of the Reagent.—Hyposulphite (hydrosulphite) of sodium is formed by the action of zinc on acid sulphite of sodium, thus:

$$3NaHSO_3 + Zn = NaHSO_2 + Na_2SO_3 + ZnSO_3 + H_2O$$

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[*] Schützenberger and Risler, Bull. Soc. Chim. [2], xix. 152; J. Chem. Soc. 1873, p. 936.

After the reaction, most of the sulphite of zinc crystallizes out, the other products remaining in solution. The liquid, which absorbs oxygen with a rapidity comparable with that of pyrogallate of sodium, may be employed directly, or it may be converted into neutral hyposulphite by adding to it an excess of milk of lime, whereby the remainder of the zinc is thrown down as oxide, together with sulphite of calcium, whilst neutral hyposulphite of sodium (Na_2SO_2) remains in solution. The neutral salt absorbs oxygen much less rapidly than the acid salt. The following mode of operating is adopted by the authors: A quantity of zinc in strips twisted so as to occupy a large bulk is placed in a wide-necked flask of 200 c. c. capacity, which is then filled with a solution of acid sulphite of sodium of 10° Baumé, fully saturated with sulphurous acid; the flask is closed with a caoutchouc stopper, perforated to allow the escape of air, and finally closed with a piece of glass rod. In about half an hour, the reaction is complete, and the solution may be at once diluted to about two litres for use if acid hyposulphite is desired. To obtain neutral hyposulphite when necessary, the contents of the flask are poured into a 1-litre flask containing 30 gms. of previously slaked quicklime, and 600 c. c. of water; the flask is filled with water and allowed to cool. When clear, the supernatant liquid, which should be feebly alkaline, is syphoned into a 2-litre flask half full of water.

Titration of the Hyposulphite.—The strength of the hyposulphite solution, whether acid or neutral, is determined by means of an ammoniacal solution of cupric oxide, which substance is reduced, first to cuprous oxide, and then to the metallic state, by an excess of the hyposulphite. Neutral or acid hyposulphite of sodium is converted by absorption of free oxygen into neutral or acid sulphite; but the authors have found that in reducing cupric to cuprous oxide, the hyposulphite takes up only half as much oxygen as it would take up if the oxygen were free, and that consequently the product of the oxidation cannot be the same. They dissolve 2·23 gms. of crystallized sulphate of copper in water, and add an excess of ammonia, and enough water to make up the bulk to 1 litre. 100 c. c. of this solution represent 1 c. c. of oxygen.

The titration of the hyposulphite may be made in an open vessel, 20 c. c. of the copper solution being employed. The point of the Mohr's burette containing the hyposulphite should be very long, so as to dip below the surface of the copper solution, and the reagent should be run in rapidly with constant stirring till the blue color changes to very pale yellow. The error due to atmospheric oxidation may be avoided by making the titration in a close vessel in a current of hydrogen or coal gas deprived of oxygen. Comparison of the two methods has shown that this error amounts to about ·5 c. c. in 20 c. c. of hyposulphite. The solution of hyposulphite is of a convenient strength when 20 to 30 c. c. of it are required to decolorize 20 c. c. of the copper solution.

The hyposulphite solution, the strength of which has been thus found, is employed at once to determine the amount of dissolved oxygen in water, by plunging the point of the burette to the bottom of a vessel containing a litre of the water, slightly colored with Coupier's blue, and running in hyposulphite till the color disappears, the two liquids being mixed with an agitator in such a way as not to disturb the surface. The free oxygen in water cannot be thus determined in an atmosphere free from oxygen, on account of the rapid loss of oxygen by diffusion; but this difficulty may be surmounted by introducing into a vessel filled with hydrogen first an excess of the hyposulphite, and then the water, and estimating the excess of hyposulphite by means of a solution of indigo of known strength, that substance being bleached by hyposulphite.

ANALYSIS OF URINE.

In making an analysis of urine, for medical purposes, great exactness is not necessary, rapidity being the chief desideratum. In taking a sample of urine for analysis, the following points should be noted: 1. Volume of urine passed in 24 hours. 2. Color and smell. 3. Reaction to litmus paper. If the urine contains suspended solid matter, this should be filtered off and examined separately.

SPECIFIC GRAVITY.

This is usually determined, and with sufficient exactness, by means of a special hydrometer, called a urinometer, giving specific gravities between 1·000 and 1·040. The specific gravity may also be determined by a specific gravity bottle which holds 100 gms. distilled water at 16°. The temperature, of course, exercises an influence upon the specific gravity, and the urine should be brought to the temperature of 16° before the specific gravity is taken. According to the researches of Siemon, a difference of 3° corresponds to a difference of about ·001 in the specific gravity of the urine, the specific gravity becoming less as the temperature rises.

TOTAL SOLIDS.

According to Neubauer, the amount of dissolved solids may be calculated with tolerable accuracy from the specific gravity. The three last places of the four decimals in the specific gravity, multiplied by 0·233, give the amount of solids, in grammes, in 1000 c. c. urine. Neubauer gives the following example:

Quantity of urine for 24 hours, 1500 c. c. Specific gravity = 1·0134. Solids in 1000 c. c. = (0·233 × 134) = 31·22 gms., or in 1500 c. c. = 46·83 gms. By the gravimetric method, to be presently described, 46·59 gms. were found in 1500 c. c. of the same urine.

Gravimetric Method.—When urine is simply evaporated to dryness, a portion of the urea is decomposed by the acid sodium phosphate present into carbon dioxide and ammonia. The latter combines with the acid sodium phosphate at ordinary temperatures, but is again decomposed at 100°, so that if urine be directly evaporated, a continual evolution of ammonia is noticed, and the amount of residue obtained is decreased by the weight of the urea destroyed. To obviate this error, Neubauer proceeds as follows: The apparatus employed consists of a circular water-bath 12 cms. high and 11 cms. diameter, shown in Fig. 44, through which passes a tube of sheet iron, 2½ to 3 cms. in diameter. *B* is of glass, *D* contains a measured quantity of sulphuric acid of known strength, and *F* contains calcium chloride. The apparatus is connected with an aspirator by the tube *E*.

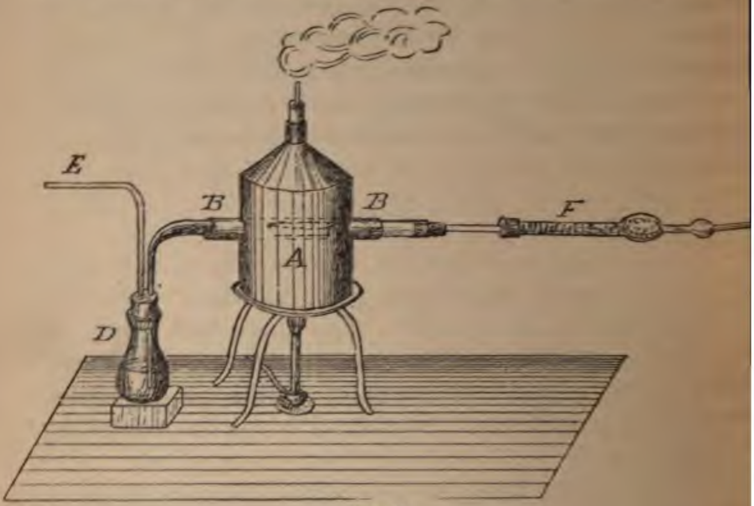

FIG. 44.

A porcelain boat, 7–8 cm. long and 1·4 cm. in width, is two thirds filled with pieces of glass, and 2 c. c. of the urine in which the determination of total solids is to be made poured over the broken glass. The boat and contents are inserted in the tube *B*, and the water in the water-bath heated to boiling, while a stream of air is drawn through the apparatus. In about three hours, the operation is ended. The porcelain boat is taken out, allowed to cool under a desiccator, and weighed. The difference between the weight before and after the operation is total solids. To the amount so obtained, the urea corresponding to the ammonia given off is still to be added. The ammonium carbonate adhering to the glass tube is washed into the flask containing the acid, and the excess of acid found by $\frac{n}{10}$ alkali.

$$\text{c. c. } \frac{n}{10} \text{ acid} \times \cdot 0030 = CN_2H_4O$$

Total Saline Matter.

Ten c. c. of the urine is evaporated to dryness in a platinum dish, and carefully heated over a lamp until no more gas is given off. The mass is treated with hot water, and filtered through a small filter. The colorless filtrate is evaporated to dryness, heated to redness, and weighed. The filter, with its contents, is dried, burned, and the residue, after deducting the filter-ash, added to the amount already found.

CHLORINE.

Mohr's Method.—5·85 c. c. of the urine is run into a platinum evaporating dish, 1 gm. potassium nitrate free from chlorine added, the whole evaporated to dryness, and heated over the lamp till perfectly white. The mass is dissolved in water, and nitric acid added until the solution is neutral or only faintly alkaline. Two or three drops of a saturated solution of potassium chromate are then added, and $\frac{n}{10}$ silver solution run in until the red color produced no longer disappears on stirring the liquid. The c. c. of silver solution, divided by 10, gives the per cent of sodium chloride, the form in which the chlorine is usually calculated.

Instead of 5·85 c. c. of urine, 10 c. c. may be taken, and then c. c. of $\frac{n}{10}$ silver solution × ·0035457 = Cl.

The organic matter, which interferes with the application of Mohr's method may, according to Pribram,* be destroyed by adding a solution of potassium permanganate to 10 c. c. of the urine, until the pink tint appears, boiling and filtering. The chlorine is then determined in the filtrate.

Volhard's Method.—The urine is evaporated to dryness with potassium nitrate, heated until the residue is white, and the chlorine in the residue estimated by adding an excess of $\frac{n}{10}$ silver nitrate, then a little ferric sulphate and $\frac{n}{10}$ potassium sulphocyanide until the solution takes a faint brownish-red color. (See page 168.)

UREA.

Liebig's Method.—This method is founded upon the fact that mercuric nitrate precipitates urea from its solution as a white powder which contains one equivalent urea to four equivalents of mercury. The indicator used is sodium carbonate. As long as no excess of mercury is present, this gives a white precipitate; but when the mercury is in excess, a yellow precipitate is formed.

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* Zeitschrift f. An. Chem. 9, 428.

Solution of Mercuric Nitrate.—77·2 gms. mercuric oxide is dissolved in the least possible quantity of nitric acid, and diluted to a litre. A sufficient excess of acid to keep the liquid clear upon diluting should be present, but any beyond this must be carefully avoided, as the white precipitate of urea and mercury is soluble in nitric acid.

Phosphoric acid and chlorides interfere with the accuracy of the method, and must be removed before the urea is determined; 50 c. c. of the urine is mixed with 50 c. c. of baryta-water, shaken and filtered; 20 c. c. of the filtrate, = 10 c. c. urine, are taken, the excess of barium hydrate saturated with nitric acid, and sufficient $\frac{n}{10}$ silver solution added to exactly precipitate the chlorine present. The amount of chlorine having been determined in a previous experiment, this is easily calculated. Without filtering, the solution is brought under the mercury burette, and the mercury solution run in until a drop of the fluid tested with a drop of sodium carbonate upon a watch-glass gives a yellowish precipitate. The analysis may be checked by dissolving ·1 gm. urea in water, and adding 10 c. c. of the mercury solution. A drop of the solution, treated with a drop of sodium carbonate, gives a precipitate, the color of which serves as a guide in the analysis of the urine.

c. c. mercury solution divided by 10 = % urea

If the urine contains albumen, this must be separated by boiling for a few minutes with a few drops of acetic acid, and decanting from the precipitate, then filtering and determining the urine in the filtrate. If ammonium carbonate is present, the solution must be heated after the addition of barium hydrate, to drive off the free ammonia, and, after the removal of the chlorine, the urea estimated in the ordinary way.

By Conversion of the Urea into Nitrogen Gas, and Measuring the Volume.—Knop* converts the urea in urine into nitrogen gas, and calculates the amount of urea from the volume. The process has since been modified by Hüfner,† who proceeds as follows:

The apparatus used is shown in Fig. 45: *a* should have a capacity of 5–8 c. c., and is connected with *c* by the cock *b*, having a tolerably large perforation. The vessel *d*, which may be made from the upper part of a bottle, is connected tightly with *c* by means of a cork; *e* is a eudiometer tube 2 cm. wide, 30 cm. long, and divided in $\frac{1}{5}$ c. c.

Bromized Soda Solution.—The solution for decomposing the urea is made by dissolving 100 gms. sodium hydrate in 250 c. c. water, and adding 25 c. c. of bromine to the cold solution; 50 c. c. of this solution is diluted with 200 c. c. water for use. It is best to prepare a fresh quantity of this solution each time.

Take 10 c. c. of the urine and dilute to 40–50 c. c. By the aid of a funnel tube, the vessel *a*, together with the bore of the cock (the content of these in c. c. being known), is filled with the urine, and the cock turned. The bromized soda solution, diluted with an equal volume of water, is now poured into *c*, until it has a depth of 2 cm. in the vessel *d*. If any urine remains in *c*, the urea it contains is decomposed, and nitrogen gas given off. After the evolution of gas has ceased, the eudiometer is filled with water and inverted over the upper end of *c* in the vessel *d*. The cock *b* is now opened, when the bromized soda solution sinks into *a*, on account of its high specific gravity, and, mixing with the urine, decomposes the urea. The nitrogen rises into the

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* Chem. Centralblatt, 1860, 274. † Jour. f. Prak. Chemie, cxi. 1.

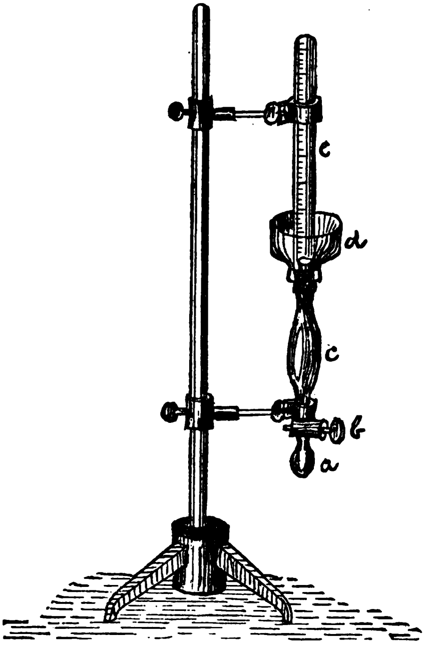

FIG. 45.

eudiometer, and after a few hours its volume is determined, first removing it to a cylinder filled with water. According to Russell and West,* ·1 gm. urea produces, by its decomposition, 37·1 c. c. nitrogen gas, and the calculation can be made upon this basis. In ordinary cases, no correction of the volume of gas for temperature, pressure, etc., need be made, as the amount of nitrogen dissolved by the fluid about compensates for the increase of volume due to moisture. When correction is made, the following formula is employed, calculating 1 gm. urea to give 370 c. c. nitrogeng as at 0°C, and 760 mm. barometric pressure.†

$$p = \frac{100\, v\, (b - b')}{760{,}370,\ a\, (1 + 0{\cdot}003665\, t^\circ)}$$

a = volume of urine used.
b = volume of gas read off.
v = height of the barometer.
t = temperature.
b' = tension of water vapor for the temperature t.

If albumen be present in the urine, it should be precipitated by heating with 2 or 3 drops of acetic acid. Sugar does not interfere.

Method of Musculus.‡—Pasteur and Van Tieghem having shown that the conversion of urea into ammonium carbonate is accomplished by the action of a special torulaceous ferment, consisting of spherical balls about ·0015 mm. in diameter, Musculus has made use of the fact in the quantitative estimation of urea in urine. The ferment is preserved by filtering fermenting urine and drying the filtering-paper impregnated with the germs at 35°–40°.

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* Jour. Chem. Soc., 2 ser. xii. 749.

† Neubauer and Vogel. Analyse des Harns.

‡ Arch. Pharm. [3] v. 435 ; Fres. Zeitschrift, 15, 363.

Paper thus prepared can be kept for a month without losing any of its power of inducing the ureal fermentation.

The ferment may also be prepared by adding strong alcohol to the urine of persons suffering from catarrh of the bladder, and collecting and drying by a gentle heat the precipitate produced.

10 c. c. of the urine is taken, to which a slight excess of sodium carbonate is added, and then a few drops of litmus. The solution is diluted 10 times with water, exactly neutralized with dilute acid, and ·2 gm. of the ferment powder added. The solution is placed on a water-bath, and heated to 35°–40° for an hour, at the end of which time the urea is completely converted into ammonium carbonate, whose amount may be estimated by normal acid, and from it the urea calculated.

ESTIMATION OF PHOSPHORIC ACID.

The solutions used are the same as those described under phosphoric acid.

50 c. c. of urine are taken, to which 5 c. c. of sodium acetate are added, and the titration finished, after treating the urine by adding the solution of uranic acetate in the usual manner.

The estimation is sharper if the phosphoric acid is first precipitated by magnesia mixture, then washed with ammonia water, dissolved in acetic acid diluted to 50 c.c., 5 c.c. sodium acetate solution added, and the solution titrated with standard uranic acetate.

SULPHURIC ACID.

This is determined with $\frac{n}{10}$ barium chloride, using the filtering pipette. (See page 241.)

SUGAR.

The sugar is determined by diluting 10 c. c. of the urine to 200 c. c., and running it from a burette into 10 c. c. copper solution, diluted with 40 c. c. water, and heated to boiling in a porcelain evaporating dish. The diluted urine is added until the blue color of the copper solution disappears completely. (See Sugar.)

AMMONIA.

100 c. c. of the urine is neutralized, 10 c. c. normal alkali added, and the solution boiled until no more ammonia escapes. Care must at first be taken that the solution does not boil over, as considerable frothing generally occurs. All the combined ammonia is in this way expelled, the potassium or sodium of the normal alkali taking its place. Urea is likewise decomposed, producing ammonia and carbon dioxide, which latter unites with the potassium to form a carbonate.

The splitting up of the urea in no way interferes with the alkalinity of the solution, however, since the caustic alkali is merely changed to carbonate. After all the ammonia is driven off, the free alkali remaining is found by normal acid and litmus paper.

URIC ACID.

500 c. c. of the urine is acidified with 5 c. c. sulphuric or hydrochloric acid, and set aside for 1 or 2 days in a cold place. The uric acid is deposited in small crystals, which are generally highly colored. They are filtered through a small funnel, the neck of which is stopped with a small loosely-fitting plug of fine asbestos. Any crystals remaining in the beaker are detached with a feather and washed on the filter with a portion of the clear filtrate. They are then washed with cold water (using the smallest quantity possible) until the filtrate produces no turbidity with silver nitrate. The crystals are now dissolved in a little solution of pure sodium hydrate, washed into a beaker, and the asbestos carefully washed. The solution is diluted considerably, acidified with sulphuric acid, and titrated with permanganate.

c. c. $\frac{n}{10}$ permanganate × ·0075 = uric acid

The uric acid is not entirely insoluble in the acid fluid, and a small part of it remains in solution (according to Schwannert, ·0048 gm. for every 100 c. c.). As an offset to this, the crystals which are deposited always contain coloring matter, which also decolorizes permanganate and rectifies the error to a greater or lesser degree. To make the analyses comparable, they should, of course, always be made in the same way. All methods must be imperfect until a plan for completely separating uric acid free from coloring matter has been devised.

For further information upon the determination of uric acid in urine, see Liebig's Annalen, 163, 153; 165, 315; Supp. Bd. 2, 313. Fresenius, Zeitschrift, 7, 516; 11, 234; 14, 206; 16, 371; 9, 538. Berichte der Deutschen Chem. Gesellschaft, Bd. 5, 410. Neubauer and Vogel's Analyse des Harns, and Mohr's Titrirmethode.

ALBUMEN.

Bœdeker's Method.

The method is based upon the precipitation of albumen from an acetic acid solution by potassium ferrocyanide, 211 parts ferrocyanide precipitating 1612 parts albumen. Not less than 1½ to 2 % of albumen should be present.

Ferrocyanide Solution.—Made by dissolving 1·309 gms. in a litre of water; 1 c. c. = ·01 gm. albumen.

50 c. c. of the urine is mixed with an equal volume of acetic acid, and a burette filled with the solution. 10 c. c. are run into a beaker containing 10 c. c. of the ferrocyanide solution, mixed, and poured upon a small filter which has been previously moistened with acetic acid, and washed with boiling water. If the filtrate be yellow and clear, the ferrocyanide is in excess, and a drop of the urine added to it will produce a precipitate. If the fil-

trate be turbid and the filtration slow, the albumen is in excess, and often in such case both urine and ferrocyanide produce a precipitate.

A second trial is now made, using 10 c. c. and more or less ferrocyanide, being guided in this by the result of the previous trial, and the analysis is again repeated if necessary, using 10 c. c. urine each time, until the filtrate from the precipitate gives no cloudiness upon the addition of urine or ferrocyanide. Sutton gives the following example: "50 c. c. of urine, passed by a patient suffering from Bright's disease, were mixed with the like quantity of acetic acid, and tested as follows:

	Urine.	Ferrocyanide.	In Filtrate,	
			Urine gave	Ferrocyanide gave
1.	10 c. c.	10 c. c.	0	precip.
2.	10 "	20 "	precip.	0
3.	10 "	15 "	0	precip.
4.	10 "	17·5 "	0	faint precip.
5.	10 "	18 "	0	0

Therefore the 10 c. c. of the diluted urine = 5 c. c. of the original secretion, contained ·18 gm. albumen, or 36 parts per 1000" = 3·6 %.

GRAVIMETRIC ESTIMATION OF ALBUMEN.

The volumetric method is not very exact, and it is well to supplement it with a gravimetric estimation, which is made as follows:

A quantity of urine is taken, which contains about ·2 to ·3 gms. albumen. If this requires less than 100 c. c. urine, it should be diluted to that volume with water. The urine is brought to boiling in a beaker glass, when, if it contains sufficient free acid, the albumen coagulates. If this is not the case, a drop or two of acetic acid may be added, but care must be taken not to use an excess, as this will redissolve a portion of the albumen.

The precipitate is now allowed to settle, and the clear fluid poured upon a weighed filter, and, after it has passed through, the albumen is added. When all the fluid has run through, leaving the albumen behind, it is washed into the point of the filter by a stream of hot water, the beaker is cleaned from adhering particles by a feather, and the filter and contents washed with hot water until the filtrate produces no turbidity in solution of silver nitrate. The filter, with its contents, is dried at 100° until it no longer loses weight, dried over sulphuric acid and weighed. The difference in the weight of the filter before and after the operation is albumen.

For further information upon the analysis of urine, the student is referred to Neubauer and Vogel's "Analyse des Harns."

ESTIMATION OF TANNIN.

Methods for the estimation of tannin are only valuable for technical purposes, and can lay no claim to scientific accuracy.

HAMMER'S METHOD.*

This method is based upon the difference in specific gravity of the solution before and after the removal of the tannin. The tannin is removed by shaking the bark, or other solution, with pulverized raw hide which absorbs it. The amount of contained tannin is found by comparison with a table given below.

PREPARATION OF THE BARK OR OTHER EXTRACT.

About 40 gms. of the substance is reduced to a tolerably fine powder by an appropriate method, boiled with water, filtered, and well washed; or the residue may be put in a strong press and exhausted. In the latter case less water is required. If the substance contains a small percentage of tannin, more than 40 gms. may be used, and with galls or other substances rich in tannin, a smaller quantity suffices. The solution is poured into a graduated 250, 500, or 1000 c. c. flask, cooled to 15° by placing in spring water, and diluted to the containing mark. The specific gravity of a portion is then found either by filling a specific gravity bottle, and weighing, or by means of a hydrometer capable of indicating differences of ·0004.

Preparation of the Powdered Raw Hide.—A piece of thick hide, from which the hair has been removed, is treated with water as long as any thing is extracted, stretched over a hoop, dried by the aid of a gentle heat, and then rasped to powder with a coarse file, and preserved in a stoppered bottle. For the removal of 1 part tannin, about 4 parts powdered hide must be added to the solution. Before being used, the pulverized hide must be moistened with water and pressed. After the specific gravity of a portion of the aqueous extract has been determined, another portion is to be shaken with some of the powdered hide, the solution filtered, and the specific gravity again taken. The percentage of tannin corresponding to each specific gravity is then found from the table, and the second subtracted from the first, the result being the percentage of tannin contained in the extract. As the volume of the solution is known, the absolute weight of tannin may be easily calculated, and from this the percentage contained in the bark.

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* Jour. für Prak. Chemie, 81, 159.

TABLE.

Specific gravity of Tannin Solutions at 15°.

Per cent of Tannin.	Specific Gravity.	Per cent of Tannin.	Specific Gravity.	Per cent of Tannin.	Specific Gravity.
0·0	1·0000	1·7	1·0068	3·4	1·0136
0·1	1·0004	1·8	1·0072	3·5	1·0140
0·2	1·0008	1·9	1·0076	3·6	1·0144
0·3	1·0012	2·0	1·0080	3·7	1·0148
0·4	1·0016	2·1	1·0084	3·8	1·0152
0·5	1·0020	2·2	1·0088	3·9	1·0156
0·6	1·0024	2·3	1·0092	4·0	1·0160
0·7	1·0028	2·4	1.0096	4·1	1·0164
0·8	1·0032	2·5	1·0100	4·2	1·0168
0·9	1·0036	2·6	1·0104	4·3	1·0172
1·0	1·0040	2·7	1·0108	4·4	1·0176
1.1	1·0044	2·8	1·0112	4·5	1·0180
1·2	1·0048	2·9	1·0116	4·6	1·0184
1·3	1·0052	3·0	1·0120	4·7	1·0188
1·4	1·0056	3·1	1·0124	4·8	1·0192
1·5	1·0060	3·2	1·0128	4·9	1·0196
1·6	1·0064	3·3	1·0132	5.0	1·0201

LÖWENTHAL'S METHOD.*

The following solutions are used :

1. An $\frac{n}{10}$ solution of potassium permanganate.
2. A solution of indigo carmine, or "precipitated indigo," containing 5 gms. per litre.
3. A solution of glue made by swelling 25 gms. with water, afterwards dissolving in hot water, diluting to a litre, and saturating with common salt.
4. A saturated solution of salt, to which is added 50 c. c. hydrochloric acid (sp. gr. 1·12) per litre.

5 gms. of galls or 10 gms. bark are boiled with water repeatedly, and the filtrate diluted to a litre. To 20 c. c. of this filtrate 25 c. c. of the indigo solution are added, then 20 c. c. of the acid solution of salt, the volume is brought to 600 or 700 c. c. by addition of water, and $\frac{n}{10}$ permanganate run in until the color becomes pure yellow. A second portion of 100 c. c. of the bark solution is now taken, 50 c. c. of the glue solution added, and, after mixing the two thoroughly, 100 c. c. of the acid salt solution. The mixture is allowed to stand over night and filtered.

To 50 c. c. of the filtrate, 25 c. c. of indigo solution is added, the solution diluted to 600–700 c. c., and titrated with permanganate until the yellow color makes its appearance. The difference between the amounts of permanganate represents the tannin.

According to Oser, 1 c. c. permanganate = ·006236 gms. oak bark tannin. Or,

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* Jour. für Prak. Chemie, 81, 150 ; Fres. Zeit. 16, 33 ; ib. 201.

According to Neubauer, 1 c. c. permanganate = ·004155 gms. tannin of galls.

Löwenthal, however, remarks that the determinations made by his method can only be compared with one another when the substances examined are of the same kind; for example, results obtained on a sample of sumach and one of nutgalls are not comparable directly, but only those from sumach *inter se*, and galls *inter se*.[*]

WATER ANALYSIS.

Ordinary water used for drinking and cleansing purposes contains a number of impurities, some of which, to a greater or less extent, unfit it for use. These are different in amount and in kind according to the source from which the water is derived. Rain water, which falls after the atmosphere has been purified by previous showers, is the purest natural water. It always contains a little ammonia, however, as well as dissolved oxygen, nitrogen, and carbon dioxide, which are taken up from the air. Well water always contains impurities which differ in amount and kind according to the nature of the soil through which the water flows. If this contains much lime and magnesia, these are dissolved and the water becomes "hard." If iron be present, the water dissolves it, and is said to be "chalybeate." Water percolating through a marshy soil becomes saturated with organic matter. The purest well water is found in sandy soils, the constituents of which are nearly insoluble. River and spring water, such as is used for supplying cities and towns, is generally purer than well water. River water is, however, often very much contaminated by the admixture of sewage, especially in passing through a large manufacturing district. The sketch of the analysis of water here given should be supplemented by consulting the works of Kubel-Tiemann, Reichardt, and Wanklyn.

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[*] So many other methods for the estimation of tannin have been proposed, that it would take up too much space to enumerate them. For further information, the following articles may be consulted: Fres. Zeitschrift, 1, 104; 2, 287; 2, 419; 3, 125; 3, 126; 7, 130; 10, 1; 15, 112; 16, 123. Ber. d. Deut. Chem. Gesell. 9, 78; 9, 730. Chem. News, xxix. 109; xxix. 169; xxx. 16; xxx. 51; xxxii. 11; xxxii. 370.

COLLECTION OF THE SAMPLE.

It is best to collect the sample in glass bottles with glass stoppers. The green glass bottles used for acids answer the purpose very well. If the water is taken from a pump, the contents of the pump barrel should first be emptied. If from a spigot, the water in the pipe is first allowed to flow off. If the water is taken from a spring or river, the bottle must be rinsed two or three times with the water, immersed, filled, stoppered, and withdrawn. At the time of taking the sample, the color, smell, and taste are to be noted (best by heating a portion to 35° to 40°), and also any surrounding circumstances which might influence the purity, as, for instance, the nature of the soil, proximity of stables, outhouses, etc.

SUSPENDED MATTER.

This is found by filtering a measured volume of the water (the bottle containing which should be previously shaken) through a weighed filter, washing with distilled water (the washings are collected separately), drying at 120° in the air-bath until it ceases to lose weight, and weighing. The suspended inorganic matter may be found by burning the filter and contents and subtracting the filter ash.

DISSOLVED SOLIDS.

These may be determined by evaporating a measured volume of the filtered water to dryness in a small evaporating dish, drying at 100° until the weight is constant, and weighing. The evaporating dish is then heated to redness until the organic matter is burned off, and again weighed. The loss is the dissolved inorganic matter.

ESTIMATION OF THE HARDNESS.

The "hardness" of water is caused by dissolved salts of calcium or magnesium, which form salts with the fatty acids of the soap, insoluble in water. As soon as the calcium or magnesium is in combination with the fatty acid, the soap dissolves as in soft water. Temporary hardness is caused by bicarbonates of calcium or magnesium; by boiling the water, these are decomposed, and simple carbonates of these metals are precipitated. Permanent hardness is produced generally by calcium sulphate, and this is difficult to remedy.

Soap Solution.—This is made by triturating 15 parts lead plaster (Emplast. plumbi) with 4 parts potassium carbonate, and dissolving out the soap formed by shaking with strong alcohol. The solution, after standing, is filtered, and diluted with a mixture of 2 volumes alcohol and 1 water, until 14·25 c. c. are equal to 50 c. c. calcium chloride solution.

Calcium Chloride Solution.—Made by dissolving ·2 gms. pure calcite in hydrochloric acid, evaporating to dryness, and diluting to a litre.

50 c. c. of the water to be examined is placed in a 250 c. c. bottle and the soap solution run in by portions of 1 c. c. at first, shaking after each addition. As soon as all the calcium or magnesium is precipitated, a lather is formed by the soap in excess. When this lather remains for 5 minutes, the operation is ended. The degree of hardness is found from the following table.* If the 50 c. c. of water require more than 16 c. c. soap solution, 25 c. c. are taken, and as much distilled water added. If the water contains much magnesium (known from the curdy appearance of the precipitate), no more than 7 c. c. soap solution should be used, and the water is diluted accordingly. The strength of the soap solution is found in the same way.

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* Sutton's Volumetric Analysis.

Table of Hardness. Parts in 100,000.

c. c. Soap Solution.	$CaCO_3$ in 100,000.	c. c. Soap Solution.	$CaCO_3$ in 100,000.	c. c. Soap Solution.	$CaCO_3$ in 100,000.	c. c. Soap Solution.	$CaCO_3$ in 100,000.
0·7	·00	·6	·43	·5	11·05	·3	·90
0·8	·16	·7	·57	·6	·20	·4	17·06
0·9	·32	·8	·71	·7	·35	·5	·22
1·0	·48	·9	·86	·8	·50	·6	·38
·1	·63	5·0	6·00	·9	·65	·7	·54
·2	·79	·1	.14	9·0	·80	·8	·70
·3	·95	·2	·29	·1	·95	·9	·86
·4	1·11	·3	·43	·2	12·11	13·0	18·02
·5	·27	·4	·57	·3	·21	·1	·17
·6	·43	·5	·71	·4	·46	·2	·33
·7	·56	·6	·86	·5	·56	·3	·49
·8	·69	·7	7·00	·6	·71	·4	·65
·9	·82	·8	·14	·7	·86	·5	·81
2·0	·95	·9	·29	·8	13·01	·6	·97
·1	2·08	6·0	·43	·9	·16	·7	19·13
·2	·21	·1	·57	10·0	·31	·8	·29
·3	·34	·2	·71	·1	·46	·9	·44
·4	·47	·3	·86	·2	·61	14·0	·60
·5	·60	·4	8·00	·3	·76	·1	·76
·6	·73	·5	·14	·4	·91	·2	·92
·7	·86	·6	·29	·5	14·06	·3	20·08
·8	·99	·7	·43	·6	·21	·4	·24
·9	3·12	·8	·57	·7	·37	·5	·40
3·0	·25	·9	·71	·8	·52	·6	·56
·1	·38	7·0	·86	·9	·68	·7	·71
·2	·51	·1	9·00	11·0	·84	·8	·87
·3	·64	·2	·14	·1	15·00	·9	21·03
·4	·77	·3	·29	·2	·16	15·0	·19
·5	90	·4	·43	·3	·32	·1	·35
·6	4·03	·5	·57	·4	·48	·2	·51
.7	·16	·6	·71	·5	·63	·3	·68
·8	·29	·7	·86	·6	·79	·4	.85
·9	·43	·8	10·00	·7	·95	·5	22·02
4·0	.57	·9	15	·8	16·11	·6	·18
·1	·71	8.0	·30	·9	·27	·7	·35
·2	·86	·1	·45	12·0	·43	·8	·52
·3	5 00	·2	·60	·1	·59	·9	·69
·4	·14	·3	·75	·2	·75	16·0	·86
·5	·29	·4	·90				

The preceding estimation of hardness gives the total; the temporary hardness may be determined by boiling a measured volume of the water in a flask with a long neck for half an hour. The water is then made up to its original volume by dilution with recently boiled distilled water, filtered, and the permanent hardness determined in 50 c. c. of the filtrate.

CHLORINE.

The presence of much chlorine in a water is partial evidence of its pollution with sewage, which always contains a large quantity of sodium chloride, and the estimation is therefore an important one. The determination may be made either by Mohr's or Volhard's process. (See Chlorine.)

Calcium, magnesium, iron, sulphuric and phosphoric acids, and other inorganic substances, may be determined by the processes described in Part II., if it is thought desirable.

ESTIMATION OF AMMONIA.

Nessler's Solution.—62·5 gms. of potassium iodide is dissolved in 250 c. c. of distilled water, and a cold saturated solution of mercuric chloride added by small portions at a time until a little of the precipitate formed remains undissolved. To this solution a cold solution of 150 gms. potassium hydrate in 150 c. c. water is gradually added, the whole made up to a litre, and allowed to stand until perfectly clear, when it may be decanted for use.

Ammonium Chloride Solution.—Made by dissolving 1·5695 gms. pure dry salt in water, and making up to a litre. 100 c. c. of this solution are then diluted to a litre for use. Of the latter solution, each c. c. contains ammonium chloride equal to ·00005 gms. ammonia (NH_3).

Dissolve about 1 gm. fused sodium carbonate in distilled water, and introduce into a retort connected with a Liebig's condenser. The beak of the retort must be pointed upwards, so that the water condensing in it may run back. Heat the water to boiling, and distil until the distillate, collected in a cylinder upon white paper, shows no yellow coloration when tested with a few drops of Nessler's solution. The water to be tested is then poured into the retort, and the distillation continued, collecting each 50 c. c. of the distillate in a separate cylinder. Nessler's solution (about 1 c. c.) is then added to each 50 c. c., and the same color is produced in a second cylinder by taking 50 c. c. distilled water free from ammonia, adding a measured quantity of the ammonium chloride solution (less than 2 c. c.), and then 1 c. c. Nessler's solution. If the colors produced in the first trial are not the same in intensity, a second trial must be made by adding more or less ammonium chloride to another 50 c. c. of distilled water. The ammonium chloride must always be added *before* the Nessler's solution.

When 50 c. c. distillate contain less than ·00001 NH_3, as shown by color comparison, the distillation is discontinued. By adding together the amounts of NH_3 found in the separate portions of distillate, the amount for the volume of water taken is found at once. The results are accurate only when but small quantities of ammonia are present.

ALBUMINOID AMMONIA.

Under this term Wanklyn and Chapman include the ammonia which may be produced from albuminous matters, contained in the water by boiling with an alkaline solution of potassium permanganate. To the contents of the retort, after the completion of the preceding estimation, 50 c. c. of a mixture of 8 gms. permanganate, 200 gms. potassium hydrate, and 1 litre of distilled water, are added, and the distillation continued. If the boiling is irregular and bumping occurs, a few pieces of pumice, recently ignited, may be introduced with good effect. The estimation of ammonia in the distillate is made as in the preceding case.

NITROGEN AS NITRATES AND NITRITES.

A portion of the water is evaporated to dryness on the water-bath, dissolved in a little distilled water, and then the nitrates and nitrites estimated by Thorpe's process, described on page 200. The ammonia in the distillate is estimated by Nessler's solution. A small fragment of lime is added to the contents of the retort to assist in expelling the ammonia. This method gives both ammonia and nitrates, and from this the amount of the former, being already found, must be subtracted.

POISONOUS METALS.

Small quantities of copper may be determined by a colorometric process described in Part II.

Small quantities of lead may be determined upon the same principle, using a solution of hydrogen sulphide in place of potassium ferrocyanide.

CONCLUSIONS.

The conclusions to be drawn from the analysis of a water depend not so much upon one determination as upon the analysis as a whole. In general, however, large amounts of chlorine, ammonia, albuminoid ammonia, and nitrates should cause a water to be looked upon as of suspicious character and unfit for drinking purposes.

The limits, ordinarily, are about as follows: Ammonia ·008, albuminoid ammonia ·01, and chlorine 2· parts in 100,000. If the water is to be used for cleansing purposes or for boilers, the determination of temporary and permanent hardness is the most important point. Late papers upon water analysis are as follows: Kämmerer, Jour. für Prak. Chem. 14, 316; ib. 322. H. Vohl, Ber. Deut. Chem. Ges. 10, 1811. See also Fres. Zeit. xv. 230, 425, 479; ib. xvi. 359, 500.

INDIGO

May be estimated by dissolving in fuming sulphuric acid, allowing to stand for some time, diluting largely with distilled water, and titrating with permanganate until the color changes from blue through green to yellow. The titration must always be conducted under the same conditions of temperature and dilution, or great irregularities occur. The permanganate is titrated against pure indigo carmine.

The details are too extensive for insertion here, and the following papers may be consulted: Chem. News, xxv. 175; Dingler's Polytech. Jour. 132, 363; 119, 114; 128, 208; Jour. Chem. Soc. 1865, 223.

ADDENDA.

SINCE this work has been in press, an important paper by Volhard upon his method for estimating silver has appeared in Liebig's Annalen, 190, 1. The author applies his method to the estimation of silver, copper, mercury, the halogens, cyanides, and sulphocyanides. For details the paper itself must be consulted, as it is too extensive to admit of an abstract here.

Another paper in the same journal, p. 211, by Grete, gives more complete directions for the estimation of carbon bisulphide by his process described on page 243 of this book.

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